Welcome to

Aakash + BYJU'S LIVE

The p-Block Elements (Group 15-18)

p-Block Elements

Group **13 to 18** of the periodic table of elements constitute the p-block.

The p-block contains **metals, metalloids, as well as non–metals.**

General **valence shell** electronic configuration **$ns^2\ np^{1-6}$**

Except He: $1s^2$

Oxidation State

- **Inert pair effect:** Due to **poor shielding** effect of the intervening **d & f** orbitals, **increased Z_{eff}** holds the **ns^2** electrons **tightly,** and hence **ns^2** electrons **do not participate** in the bonding.
- The inert pair effect predominates only in the **sixth period** of the p-block.
- The **highest oxidation state** of p-block elements = (**group number-10**)
- Down the group, **stability** of (**highest O.S. - 2**) **increases** due to inert pair effect.

Anomalous Behaviour

The **first member** of each group from 13-17 of the p-block elements **differs** in many respects from the other members of their respective groups.

This is because of their **small size, high electronegativity, and absence of d-orbitals.**

Anomalous Behaviour

The first member of the group has a **greater ability** to form (as compared to other members of the same group)

$p\pi$-$p\pi$ multiple bonds

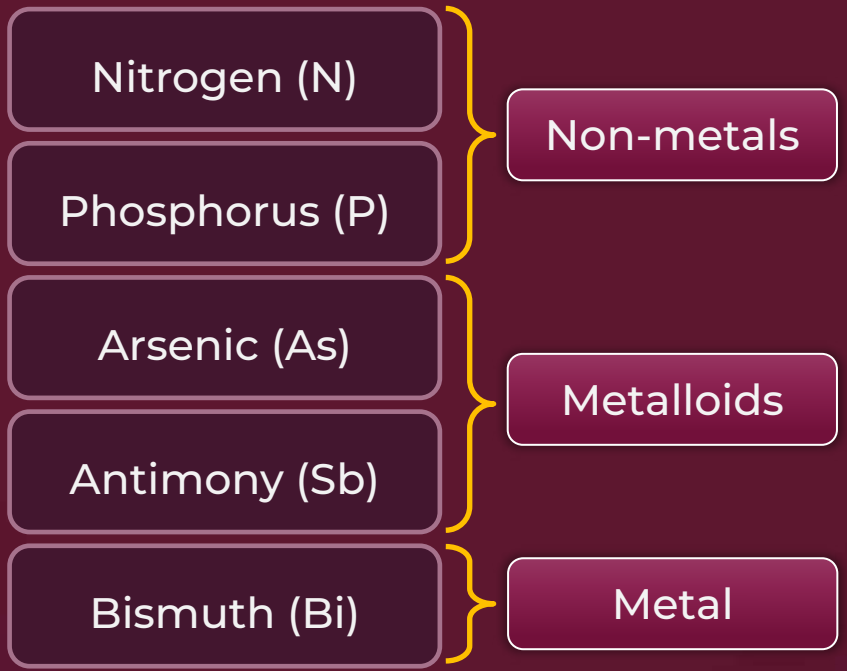
With itself

Example: C=C, C≡C, N≡N

With elements in the same period of the p-Block

Example: C=O, C=N, C≡N, N =O

Group 15 Elements



Group 15 Elements

- Occurrence
- Atomic properties
- Physical properties
- Chemical properties

Nitrogen Occurrence

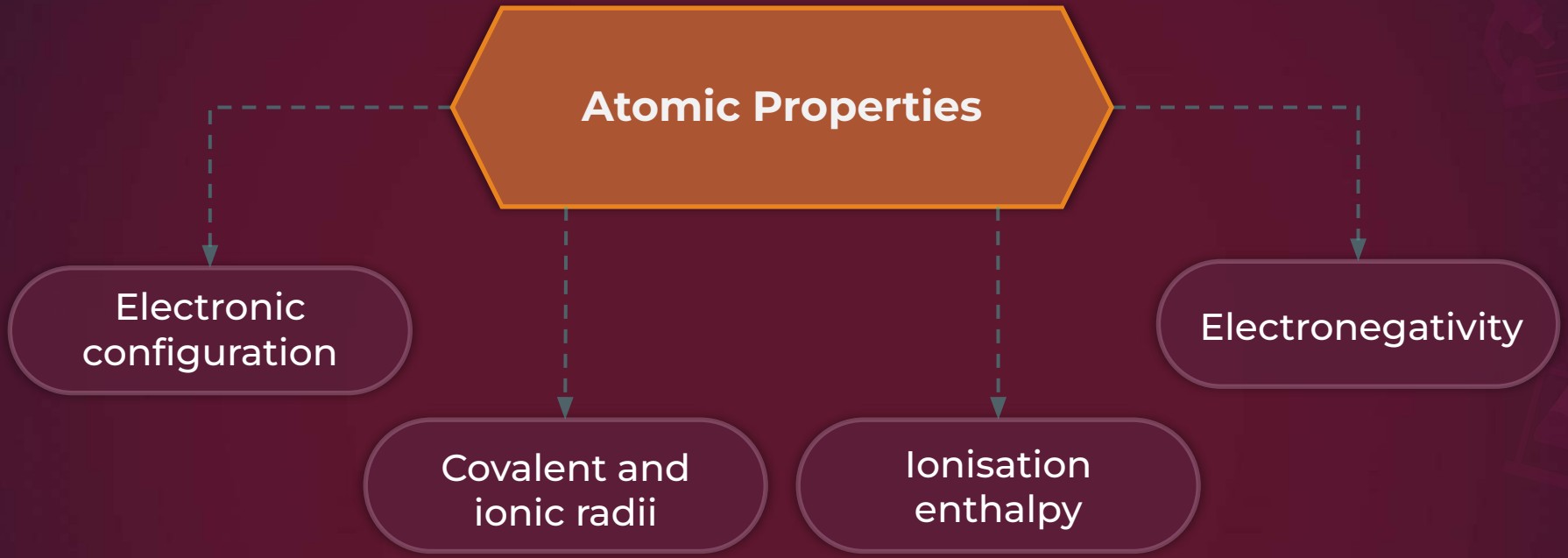
1. Molecular nitrogen comprises **78%** of earth's atmosphere by **mass**.
2. It is an essential constituent of **proteins** and **amino acids**.
3. It occurs as **sodium nitrate**, $NaNO_3$ (known as Chile saltpetre) & **potassium nitrate** (Indian saltpetre).

Phosphorus And Other Elements

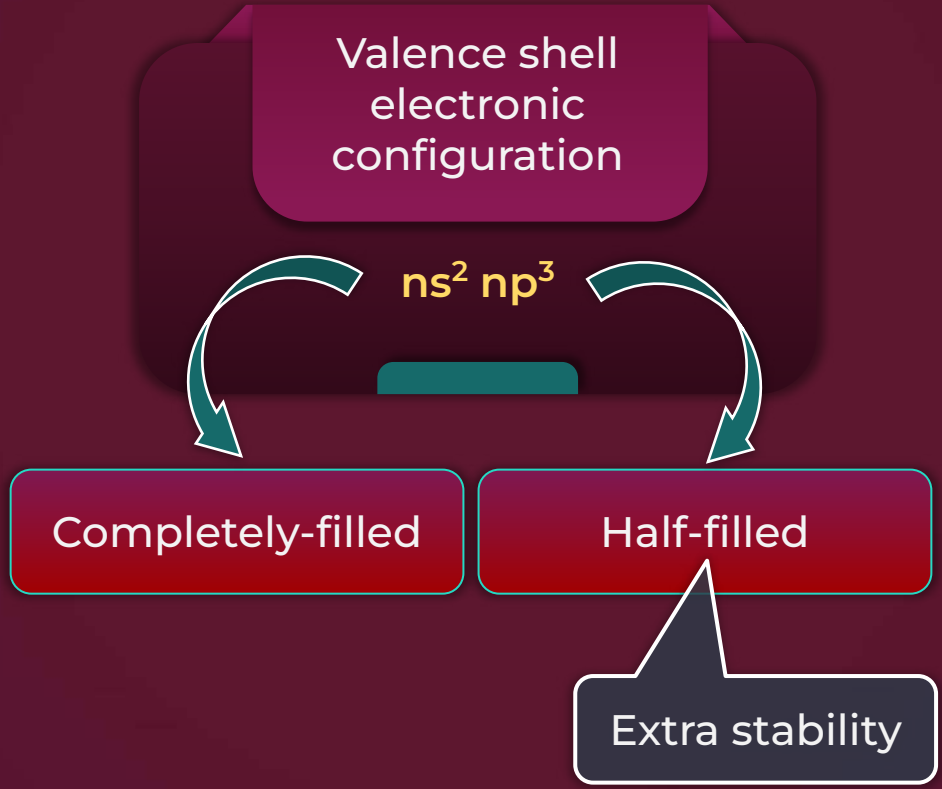
1. Phosphorus occurs in minerals of the apatite family, $Ca_9(PO_4)_6.CaX_2$ (X = F, Cl, or OH) which are the main components of phosphate rocks.

2. Phosphorus is an essential constituent of **animal and plant matter.**

Arsenic, antimony, and **bismuth** are found mainly as sulphide minerals.


Atomic Properties
Electronic configuration
Covalent and ionic radii
Ionisation enthalpy
Electronegativity

Electronic Configuration



Covalent and ionic radii

1

Down the group, ionic and covalent radii **increases**.

2

Down the group, covalent radii from N to P increases considerably, but from **As to Bi** there is only **slight increase,** because of **poor shielding effect** of d and f orbitals.

Ionisation Enthalpy

Down the group

Atomic size ↑ → Ionisation enthalpy ↓

N > P > As > Sb > Bi

I.E. of Group 15 elements ($ns^2\ np^3$) > I.E. of Group 14 elements ($ns^2\ np^2$)

Because of **extra stable half-filled p-orbital** and **smaller size**

Electronegativity

Down the group

Atomic size ↑ → Electronegativity ↓

N > P > As > Sb > Bi

In heavier elements, the difference is not that much pronounced.

Physical Properties

1. Atomicity

All the elements of group 15 are polyatomic.

2. State

N_2 is diatomic gas while all others are solids.

3. Metallic character

Down the group → Metallic character ↑

Due to decrease in electronegativity

N < P < As < Sb < Bi

Physical Properties

4. Boiling Point

Generally, down the group **boiling point increases**.

N < P < As < Sb > Bi

Sb to Bi, there is slight decrease in boiling point due to inert pair effect.

5.Melting Point

Down the group melting point
Increases from N to As
Decreases from As to Bi.

Physical Properties

6. Allotropy

It is the phenomenon where **one substance** exist in **different physical forms.**

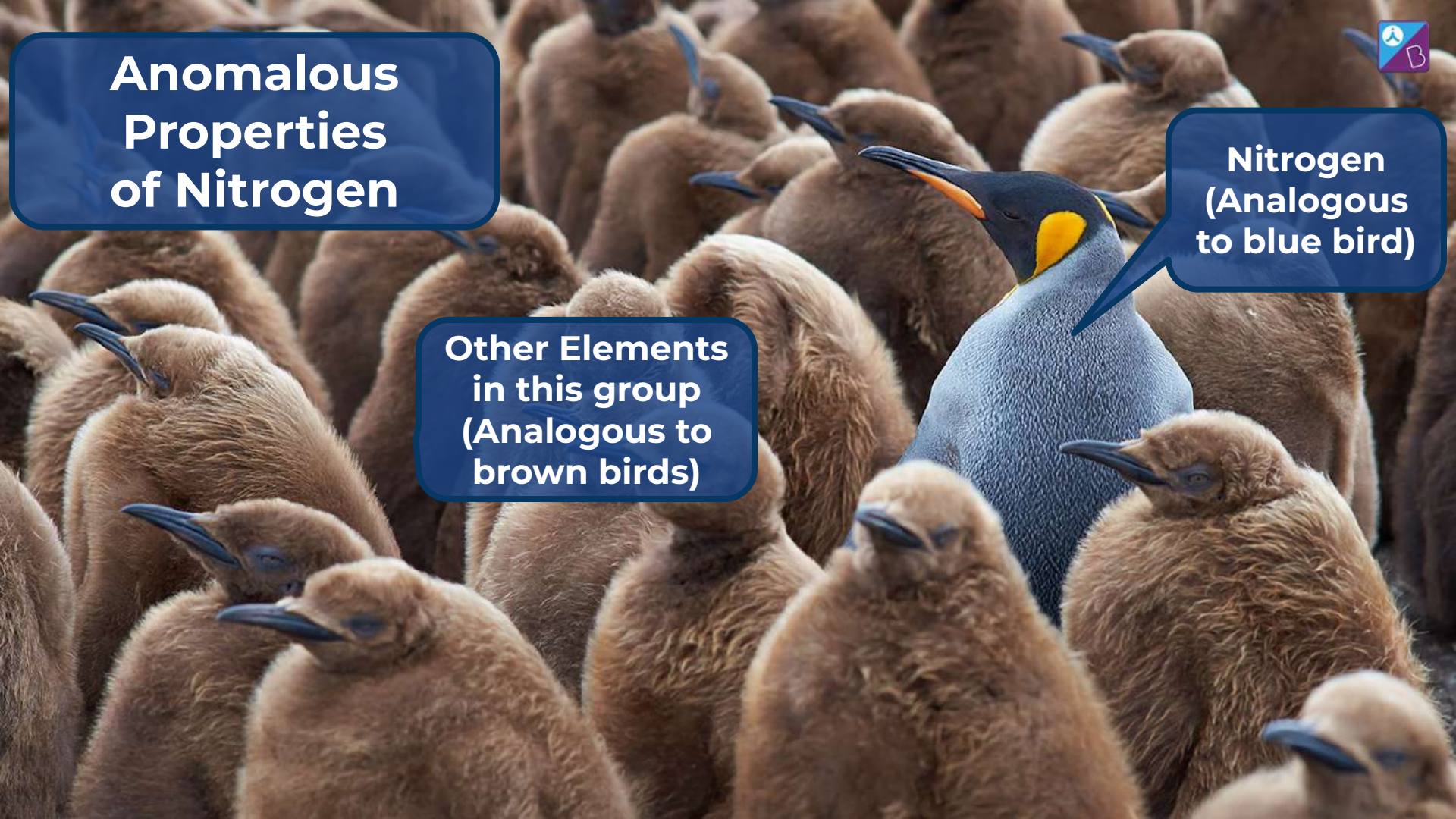
All the elements show allotropy **except nitrogen.**

Examples:

Phosphorus occurs in a **wide range** of allotropic configurations. **Red, black** and **white** phosphorus are the **three** most significant allotropic structures.

Allotropic structures of **arsenic** are **black, grey,** and **yellow.**

Yellow, metallic, and **explosive** are **three** significant allotropic structures for antimony.


Anomalous Properties of Nitrogen
Nitrogen (Analogous to blue bird)
Other Elements in this group (Analogous to brown birds)

Anomalous Behaviour of Nitrogen

The catenation tendency is **weaker** in nitrogen due to **weak N-N single bond.** Nitrogen forms **pπ-pπ multiple bonds** with itself and other elements whereas heavier elements of same group can't.

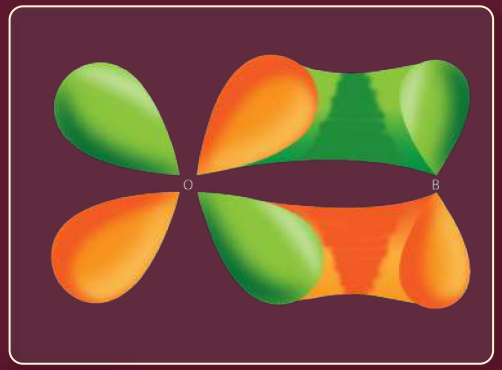
Another factor that affects the chemistry of nitrogen in the **absence of d-orbitals** in its valence shell.

Bonding And Covalency

Besides restricting its covalency to **4**, nitrogen **cannot form a pπ-dπ** bond.

It has **one s** and **three p-orbitals** for bonding

No d-orbital



Heavier elements can form

dπ-pπ bond

Eg: $R_3P=O$
or $R_3P=CH_2$
(R: Alkyl group)

Chemical Properties

- Oxidation states and trends in chemical reactivity
- Reactivity towards hydrogen (hydrides)
- Reactivity towards oxygen
- Reactivity towards halogens
- Reactivity towards metals

Oxidation States of Group 15 Elements

- **Common** oxidation state of group 15 elements are **-3, +3** and **+5**.
- The stability of **-3** oxidation state **decreases** down the group.
- Bismuth is **more stable** in **+3** oxidation state than in **+5** due to **inert pair effect**.
- Stability of **+5** oxidation state **decreases** down the group.

Stability of +5 Oxidation State

Order of stability of +5 oxidation state

P^{5+} > Sb^{5+} > As^{5+} > N^{5+} > Bi^{5+}

The only well-characterised Bi (V) compound

BiF_5

Other Oxidation States

Nitrogen

Exhibits → Large number of oxidation states from **-3 to +5**

When it reacts with oxygen

Compound	O.S. of N
NH_3	-3
N_2	0
N_2O	+1
NO	+2
N_2O_3	+3
NO_2/N_2O_4	+4
N_2O_5	+5

Note!!

Nitrogen **does not form** compounds in **+5** oxidation state with halogens

As it **does not have d-orbitals.**

Phosphorous shows **+1** and **+4** oxidation state in some oxoacids.

Disproportionation

Nitrogen

All oxidation states from **+1 to +4**

tend to disproportionate in an **acid** solution.

$$\overset{+3}{3HNO_2} \longrightarrow \overset{+5}{HNO_3} + H_2O + \overset{+2}{2NO}$$

Disproportionation

Phosphorus

All intermediate oxidation states

disproportionate into **+5 and –3**

both in **alkaline** and **acidic medium**

For Sb and Bi, the **+3** oxidation state becomes increasingly **stable**

with respect to **disproportionation**

$$\overset{+3}{4H_3PO_3} \longrightarrow \overset{+5}{3H_3PO_4} + \overset{-3}{PH_3}$$

Reactivity Towards Hydrogen

All the elements form hydrides of the type

EH_3

E = N, P, As, Sb or Bi

Properties of Hydrides

Stability order: $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Reducing character: $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

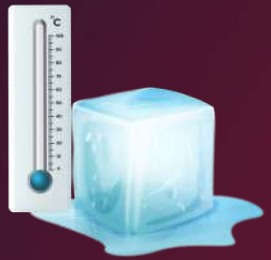
Basicity order: $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$

Properties of Hydrides

Boiling Point

PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3

van der Waals forces in bigger Sb molecules dominates the H-bonding in Ammonia



Properties of Hydrides

Melting Point

NH_3 > SbH_3 > AsH_3 > PH_3

Due to hydrogen-bonding

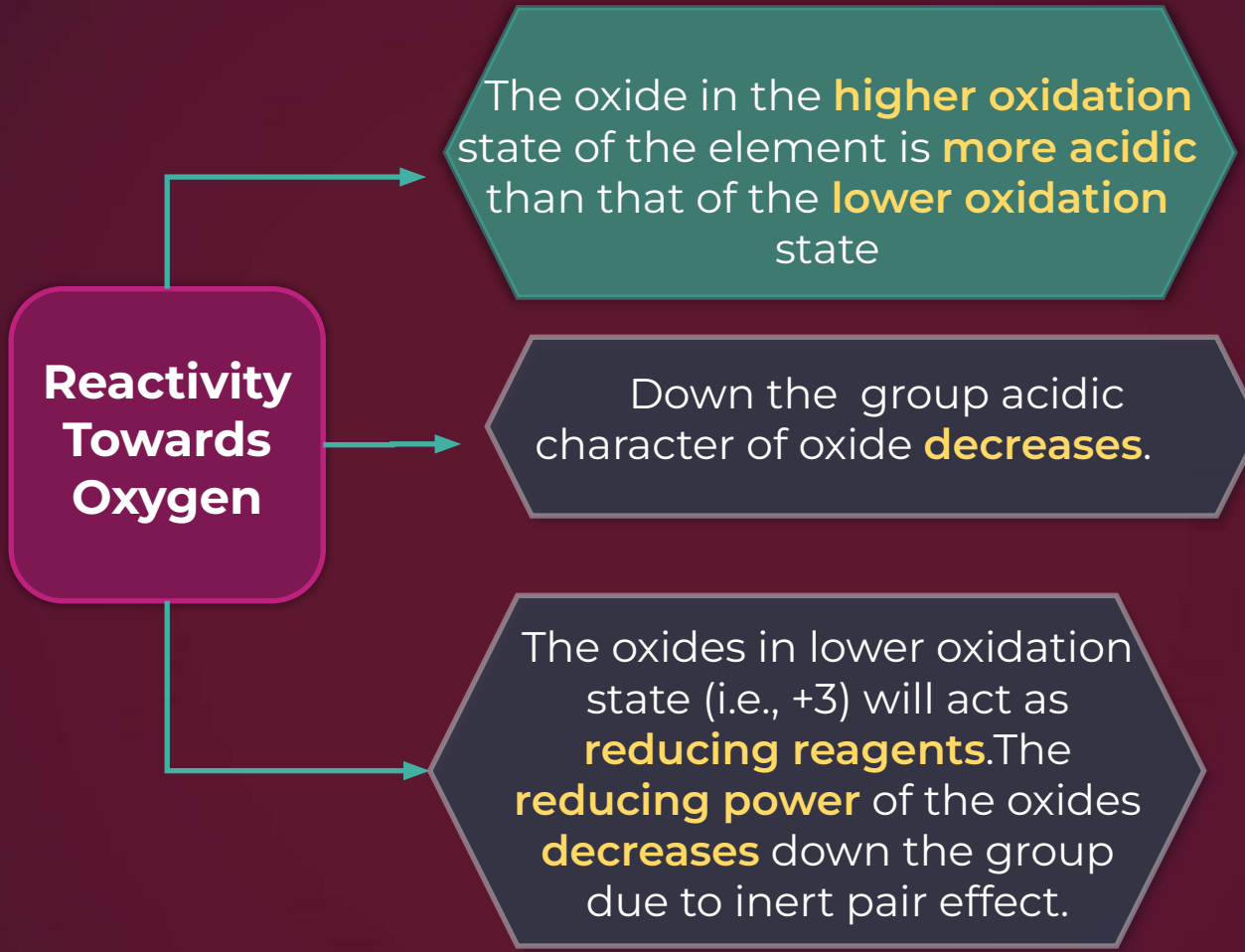
Reactivity Towards Oxygen

All the elements form two types of oxides

E_2O_3 and E_2O_5

E = N, P, As, Sb or Bi

But **nitrogen** forms various other oxides also like **NO**, **NO_2**, **N_2O**, etc.


Reactivity Towards Oxygen
The oxide in the higher oxidation state of the element is more acidic than that of the lower oxidation state
Down the group acidic character of oxide decreases.
The oxides in lower oxidation state (i.e., +3) will act as reducing reagents.The reducing power of the oxides decreases down the group due to inert pair effect.

Note

Acidic nature of oxides of nitrogen family

As the metallic nature increases on going down the group, the acidic nature of the oxides of nitrogen family (oxidation state +3) decreases.

Reactivity towards Halogens

These elements react with halogens to form two series of halides

EX_3 and EX_5

E = N, P, As, Sb or Bi

E = P, As, Sb or Bi

Reactivity Towards Halogen

These elements react to form two series of halides

EX_3 and EX_5

E = N, P, As, Sb or Bi except NX_5

- Halides are of the form **EX_3 and EX_5**.
- **Except NX_3** all trihalides are **stable**.
- **Except N** all elements form pentahalides.
- Pentahalides are **more covalent** than trihalides.
- Order of **stability of halides**: F > Cl > Br > I

Reactivity towards Metals

All these elements **react with metals** to form their binary compounds exhibiting **–3** oxidation state.

Examples

- Ca_3N_2 (Calcium nitride)
- Ca_3P_2 (Calcium phosphide)
- Na_3As_2 (Sodium arsenide)
- Zn_3Sb_2 (Zinc antimonide)
- Mg_3Bi_2 (Magnesium bismuthide)

Dinitrogen

Preparation:

In the laboratory, it is prepared by reacting aqueous solution of ammonium chloride with sodium nitrite.

$$NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$$

Industrially it is prepared from liquified air by **fractional distillation.**

Very pure form of nitrogen can be prepared by **thermal decomposition** of azides.

$$Ba(N_3)_2(s) \xrightarrow{\Delta} Ba(s) + 3N_2(g)$$

Formation of dinitrogen from sodium azide in car airbags.

$$2NaN_3(s) \xrightarrow{\Delta} 2Na(s) + 3N_2(g)$$

Physical Properties of Nitrogen Gas

- Colourless, odourless, tasteless, and non-toxic gas.
- Having very low solubility in water

Chemical Properties

N_2 is inert at room temperature because of the high bond enthalpy of N≡N bond.

Reactivity increases rapidly with rise in temperature.

At higher temperatures

With metals

It directly combines with some metals to form predominantly ionic nitrides.

$$6Li + N_2 \xrightarrow{\Delta} 2Li_3N$$

$$3Mg(s) + N_2(g) \xrightarrow{\Delta} Mg_3N_2(g)$$

With non-metals

It forms covalent nitrides

Chemical Properties

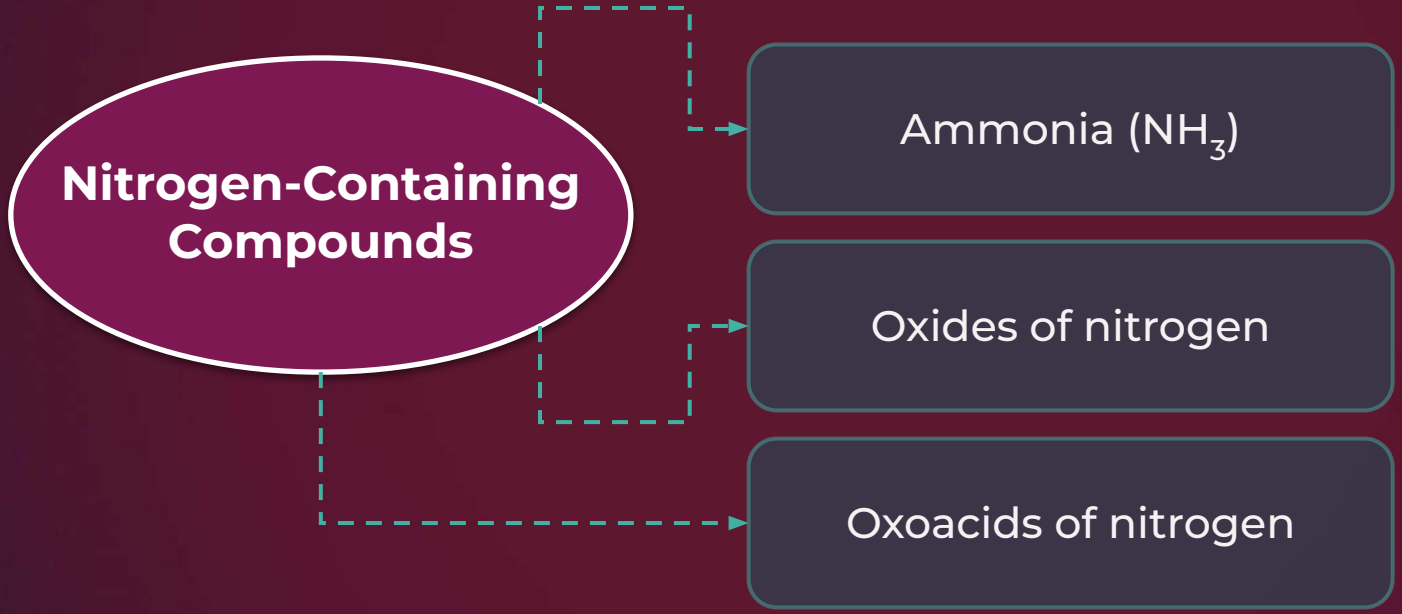
Dinitrogen combines with dioxygen only at a **very high temperature** to form **nitric oxide (NO)**

at about 2000 K

$$N_2(g) + O_2(g) \xrightarrow{\Delta} 2NO(g)$$

Uses of N_2

1. In **fertilizers.**
2. In **cryosurgery.**
3. To prevent **rancidity.**
4. As **refrigerant.**


Nitrogen-Containing Compounds
Ammonia (NH_3)
Oxides of nitrogen
Oxoacids of nitrogen

Preparation of Ammonia

1

It is formed by the decay of **nitrogenous organic matter**

$$NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3$$

$$(NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

2

Obtained from **ammonium salts** that decompose on treatment with **caustic soda** or calcium hydroxide.

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2$$

Preparation of Ammonia

1. **Haber Process :** Manufactured by **Haber's process**.

- Optimum conditions for the production of ammonia: **Pressure(20 bar - 26 bar)** and **Temperature (~723 K)**.
- **Catalyst used - Iron oxide** with small amount of **K_2O and Al_2O_3.**

2. Manufactured by the **hydrolysis** of **metal nitrides.**

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

Physical Properties of Ammonia

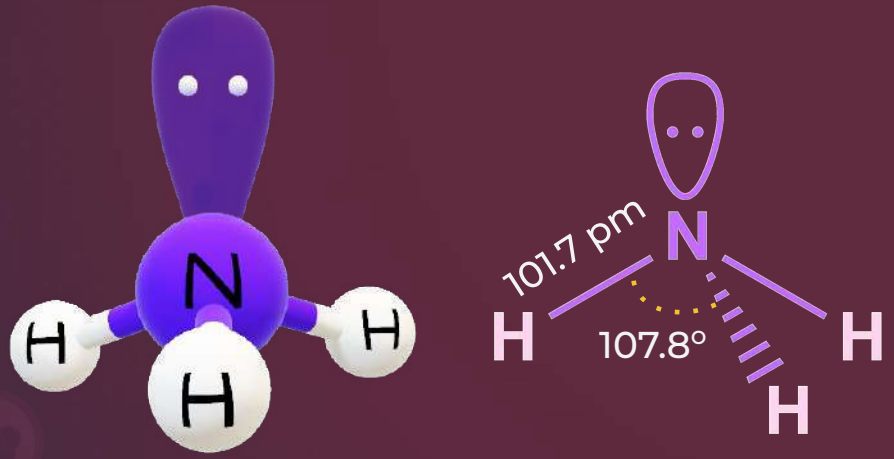
1. Colourless gas
2. Pungent odour
3. Freezing point is 195.5 K
4. Boiling point is 240 K

In solid and liquid states it is associated through **hydrogen bonds (**same as water**)**.
Due to this **association,** it has **higher melting and boiling points** than expected.

Physical Properties of Ammonia

6 Structure

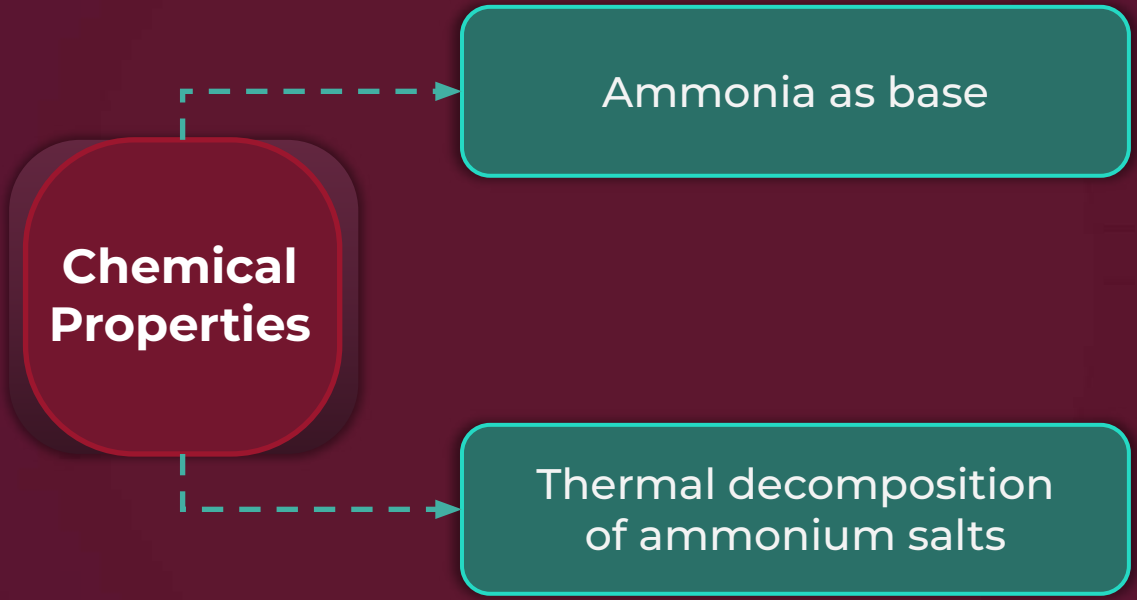
Trigonal pyramidal



7 **Highly soluble** in water

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The aqueous solution is **weakly basic** due to the formation of OH^-.


Chemical Properties
Ammonia as base
Thermal decomposition of ammonium salts

Chemical Properties of Ammonia

Ammonia as base

It forms ammonium salts with acids.

$$NH_3(g) + HCl(aq) \longrightarrow NH_4Cl(aq)$$

$$2NH_3(g) + H_2SO_4(aq) \longrightarrow (NH_4)_2SO_4(aq)$$

As a **weak base**, it precipitates the hydroxides of many metals from their salt solutions.

Chemical Properties of Ammonia

Ammonia as base

$$ZnSO_4\,(aq) + 2NH_3.H_2O\,(aq) \longrightarrow Zn(OH)_2\,(s) + (NH_4)_2SO_4\,(aq)$$

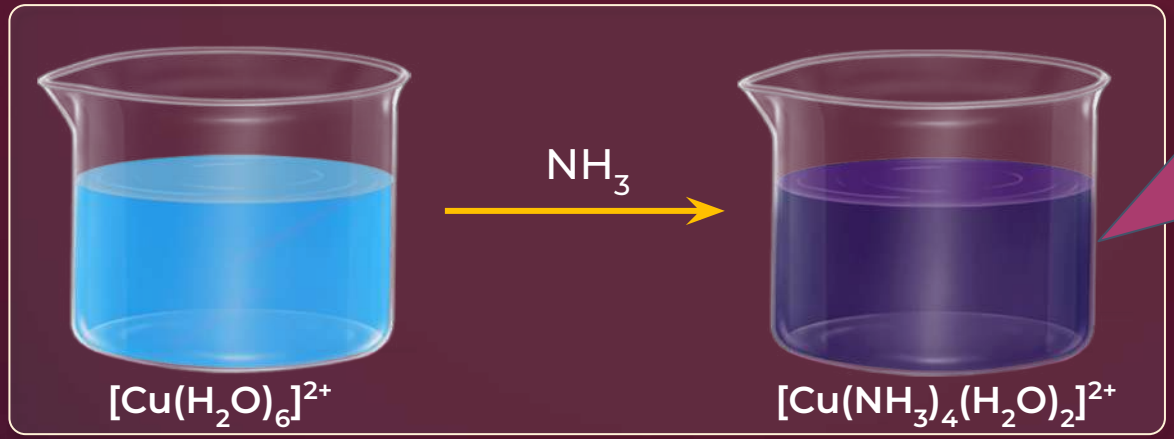
White ppt

$$FeCl_3\,(aq) + NH_3.H_2O\,(aq) \longrightarrow Fe_2O_3.xH_2O\,(s) + NH_4Cl\,(aq)$$

Brown ppt

Chemical Properties of Ammonia

Lone pair of electron on nitrogen in ammonia makes it a **Lewis base** and it helps in the **complex formation with metal ions**. Formation of ammonium complex with **Cu, Cd, Ag**, etc.



Formation of a complex of ammonia and copper results in deep blue colour

Thermal Decomposition of Ammonium Salts

- If the anion is **not oxidising**, then ammonia is evolved.

$$(NH_4)_2SO_4(aq) \xrightarrow{\Delta} 2NH_3(g) + H_2SO_4(aq)$$

- If the anion is **more oxidising**, then N_2 or N_2O is evolved.

$$NH_4NO_2(aq) \xrightarrow{\Delta} N_2(g) + 2H_2O(l)$$

$$NH_4NO_3(aq) \xrightarrow{\Delta} N_2O(g) + 2H_2O(l)$$

Chemical Properties

Reaction with halogens

When **ammonia** is in excess;

$$8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$$

When **chlorine** is in excess;

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

Uses of Ammonia

Fertilizers

Laboratory reagent

Refrigerant

Oxides of Nitrogen

Nitrogen forms a **number of oxides**

In **different** oxidation states

Oxides of Nitrogen

- Dinitrogen oxide (N_2O)
- Nitrogen monoxide (NO)
- Dinitrogen trioxide (N_2O_3)
- Nitrogen dioxide (NO_2)
- Dinitrogen tetroxide (N_2O_4)
- Dinitrogen pentoxide (N_2O_5)

Dinitrogen Oxide (N_2O)

Preparation

$$NH_4NO_3(aq) \xrightarrow{\Delta} N_2O(g) + 2H_2O(l)$$

Oxidation state

N_2O

2x	+	-2	=	0

x	=	+1

x: O.S. of nitrogen

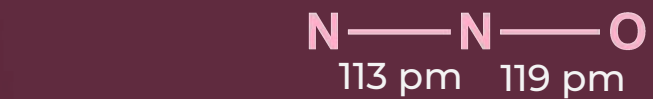
Dinitrogen Oxide (N_2O)

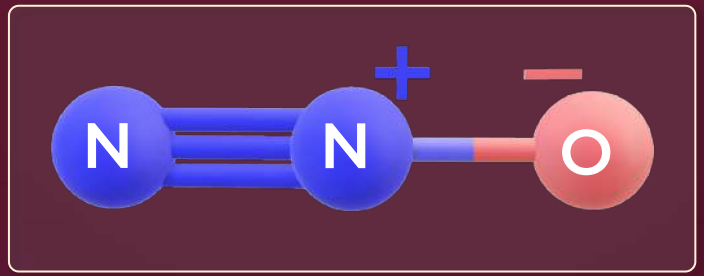
Physical appearance and chemical nature

- Stable
- Relatively unreactive
- Colourless gas
- Neutral oxide

Dinitrogen Oxide (N_2O)

Structure





Laughing Gas

Used as an anaesthetic and also known as laughing gas

Nitrogen Monoxide (NO)

Preparation

$$2NaNO_2(aq) + 2FeSO_4(aq) + 3H_2SO_4(aq) \rightarrow Fe_2(SO_4)_3(aq) + 2NaHSO_4(aq) + 2H_2O(l) + 2NO(g)$$

Nitrogen Monoxide (NO)

Oxidation state

NO

x + -2 = 0

x = +2

O.S. of nitrogen

Nature

It is an **odd electron molecule.**
Hence, the **gas** is **paramagnetic** in nature.

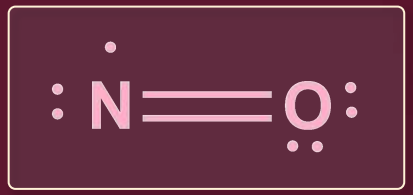
Nitrogen Monoxide (NO)

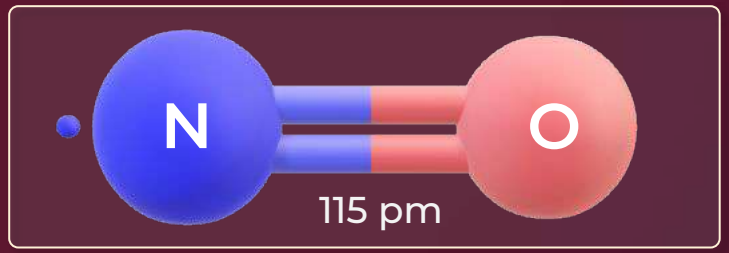
Physical appearance and chemical nature

1. Colourless gas
2. Neutral oxide
3. Reacts instantly with O_2 to give NO_2

$$2NO + O_2 \longrightarrow 2NO_2$$

Structure





Dinitrogen Trioxide (N_2O_3)

Preparation

By condensing **equimolar amounts** of NO and NO_2 together or by reacting NO with the appropriate amount of O_2.

$$NO + NO_2 \longrightarrow N_2O_3$$

$$4NO + O_2 \longrightarrow 2N_2O_3$$

Dinitrogen Trioxide (N_2O_3)

Oxidation state

N_2O_3

2x	+	3 × (−2)	=	0

x	=	+3

O.S. of nitrogen

Physical appearance and chemical nature

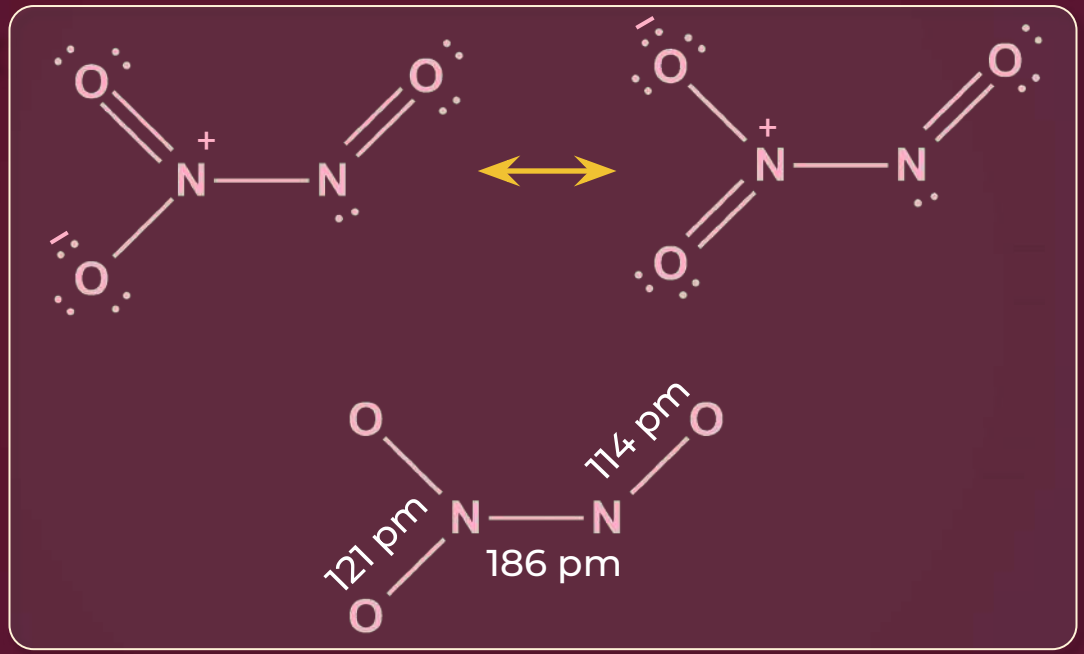
Blue solid

Acidic

It is anhydride of HNO_2

Dinitrogen Trioxide (N_2O_3)

Structure



Planar

Nitrogen Dioxide (NO_2)

1. **O.S.** of nitrogen of NO_2 is **+4**.
2. **Red-brown** poisonous gas and **very reactive**.
3. Structure: **Bent**
4. **Dimerises** into colourless **N_2O_4**.

Laboratory Method:

$$2Pb(NO_3)_2 \xrightarrow{673\ K} 4NO_2 + 2PbO + O_2$$

Yellow solid

Dinitrogen Tetroxide (N_2O_4)

Preparation

$$2NO_2(g) \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} N_2O_4(s)$$

Paramagnetic, brown

Diamagnetic, colourless

NO_2—N_2O_4 system is a **strong oxidising agent**

Dinitrogen Tetroxide (N_2O_4)

Oxidation state

N_2O_4

$2x + 4 \times (-2) = 0$

$x = +4$

O.S. of nitrogen

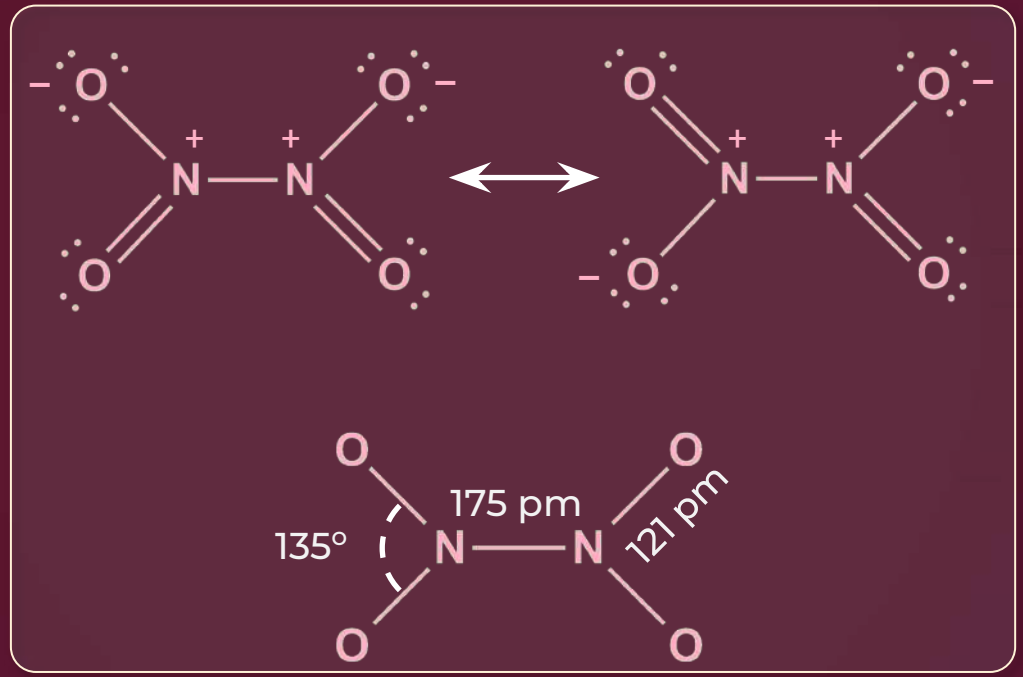
Physical appearance and chemical nature

Colourless solid/liquid

Acidic

Dinitrogen Tetroxide (N_2O_4)

Structure



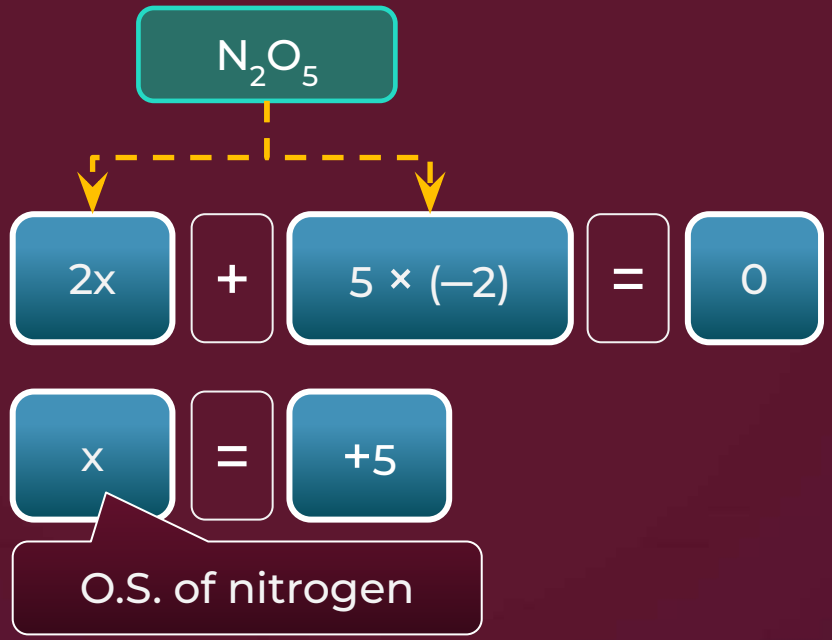
Planar

Dinitrogen Pentoxide (N_2O_5)

Preparation

$$4HNO_3(aq) + P_4O_{10}(s) \longrightarrow 4HPO_3(aq) + 2N_2O_5(s)$$

Oxidation state



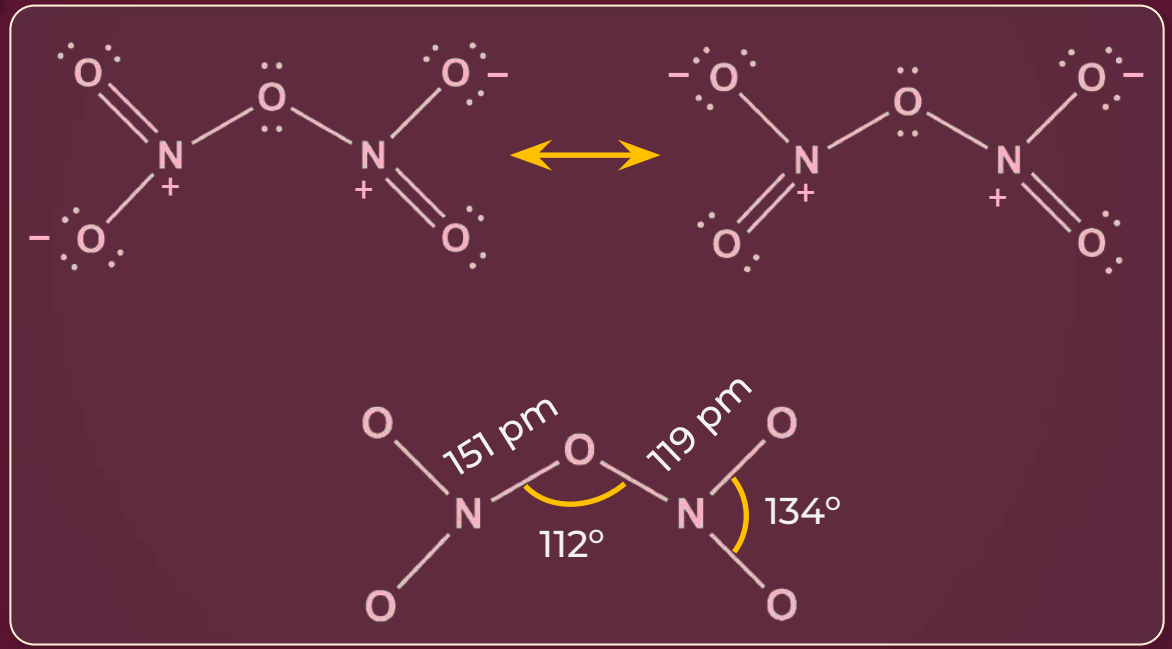
Dinitrogen Pentoxide (N_2O_5)

Physical appearance and chemical nature

1. Colourless, deliquescent solid
2. Acidic
3. Anhydride of HNO_3
4. Strong oxidising agent

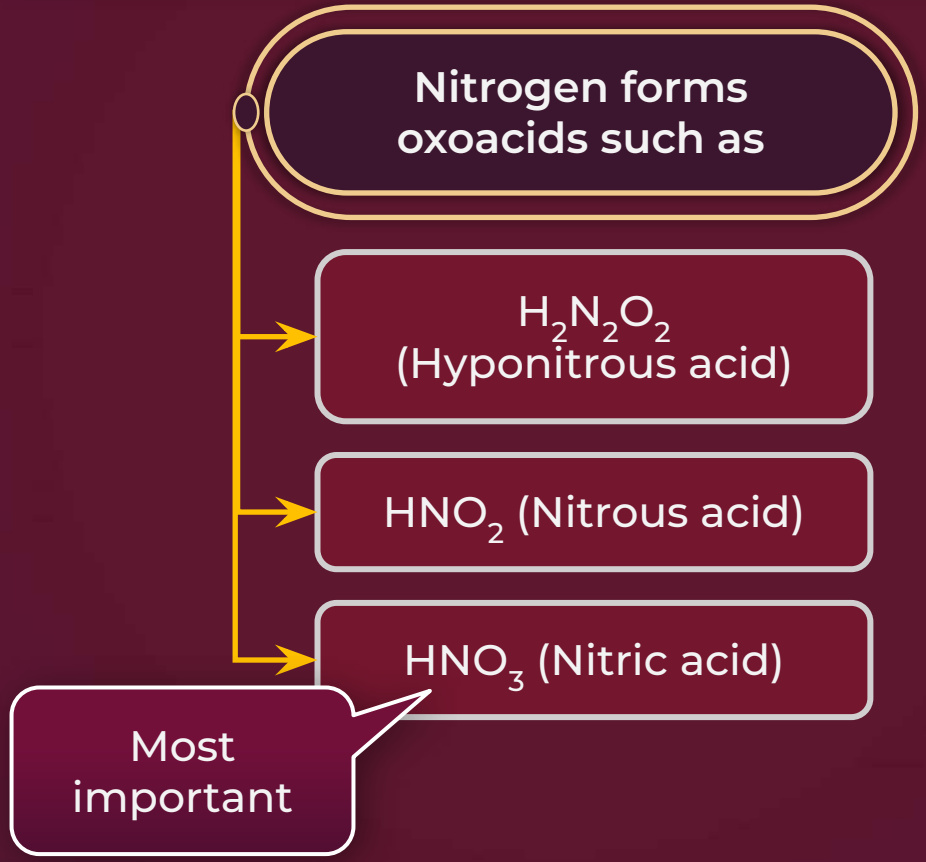
Dinitrogen Pentoxide (N_2O_5)

Structure



Planar

Oxoacids of Nitrogen



Preparation of Nitric Acid

1. **Laboratory method**: It is prepared by heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort.

$$NaNO_3(aq) + H_2SO_4(aq) \longrightarrow NaHSO_4(aq) + HNO_3(aq)$$

2. On large scale it is prepared by **Ostwald's process.**

Step 1:

$$4NH_3\,(g) + 5O_2\,(g) \xrightarrow[500\ K,\ 9\ bar]{Pt/Rh\ Gauge\ Catalyst} 4NO\,(g) + 6H_2O\,(g)$$

Step 2:

$$2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2\,(g)$$

Step 3:

$$3NO_2\,(g) + H_2O\,(l) \longrightarrow 2HNO_3\,(aq) + NO\,(g)$$

By **distillation**, aqueous HNO_3 can be concentrated up to **~68%** by mass.

Physical Properties

1. Colourless liquid

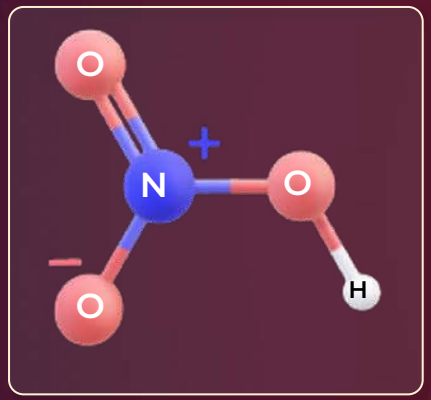
2. Freezing point is **231.4 K** and boiling point is **355.6 K.**

3. Laboratory grade nitric acid contains **~68%** of the HNO_3 by mass.

4. On exposure to **light,** it turns slightly brown because of slight decomposition into **NO_2** and **O_2.**

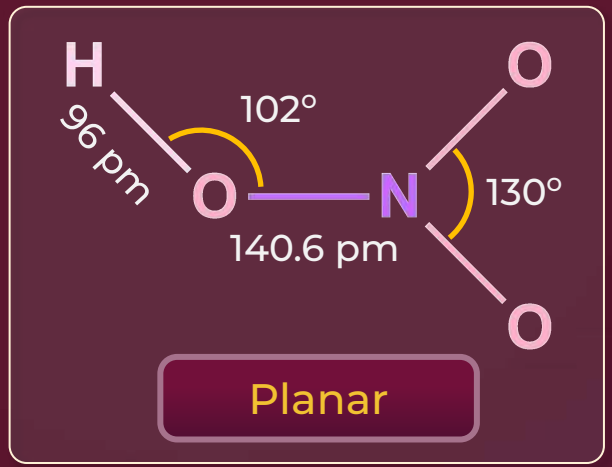
$$4HNO_3 \longrightarrow 4NO_2 + O_2 + 2H_2O$$

Physical Properties



In gaseous state

HNO_3 exists as a **planar** molecule



Chemical Properties of Nitric Acid

Reactivity

- With water
- With metals
- With non-metals and their compounds

In aqueous solution

Nitric acid behaves as a **strong acid,** releasing hydronium and nitrate ions

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

Reactivity with Metals

Concentrated nitric acid is a **strong oxidising agent.**

It attacks most metals

Except,
noble metals
Examples: **Au, Pt**

Aqua regia is a mixture of 25% conc. HNO_3 and 75% conc. HCl. Cr, Al **do not** dissolve in concentrated nitric acid because of the formation of a **passive film** of oxide on the surface.

Factors Affecting Products of Oxidation

The products of oxidation depends upon **concentration of acid**, **temperature** and **nature of material** undergoing oxidation.

$$4Zn + 10HNO_3\,(dil.) \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

$$Zn + 4HNO_3\,(conc.) \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$

Reactivity with Non-Metals

Iodine to iodic acid

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

Carbon to carbon dioxide

$$C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$$

Sulphur to sulphuric acid

$$S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

Phosphorus to phosphoric acid

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 2H_2O$$

Brown Ring Test

Depends on the ability of Fe^{2+} to reduce nitrates to nitric oxide.

Nitric oxide formed reacts with Fe^{2+} to form **brown-coloured complex**

Uses of Nitric Acid

1. To manufacture **Fertilizers.**
2. In **explosives.**
3. Etching of **metals**
4. As **Oxidizer** in **Rocket fuels.**

Allotropic Forms of Phosphorus

Important allotropic forms

- White phosphorus
- Red phosphorus
- Black phosphorus

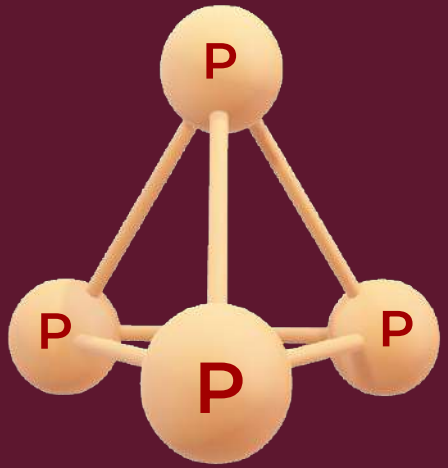
Physical Properties Of White Phosphorous

1. Translucent white **waxy** solid
2. **Poisonous**
3. **Insoluble** in water but soluble in carbon disulphide
4. **Glows** in the dark (**Chemiluminescence**)

Glows in the dark
(Chemiluminescence)

White Phosphorus

Structure



Consists of discrete **tetrahedral P_4** molecule

Chemical Properties of White Phosphorus

White phosphorus is thermodynamically **less stable.**

In an **inert** atmosphere of CO_2, it dissolves in boiling NaOH solution to give PH_3 and sodium hypophosphite (NaH_2PO_2)

$$P_4\,(s) + 3NaOH\,(aq) + 3H_2O\,(l) \longrightarrow PH_3\,(g) + 3NaH_2PO_2\,(aq)$$

Readily catches fire to give white fumes of P_4O_{10}

With **limited supply** of oxygen, it forms P_4O_6

Red Phosphorus

1. It is a polymeric chain of P_4 tetrahedra linked to form giant molecule.
2. **Insoluble** in H_2O as well as in CS_2
3. Does not ignite in air rapidly and shows **no reaction** with NaOH.
4. When **heated** at very high temperature under pressure then forms **black phosphorus.**

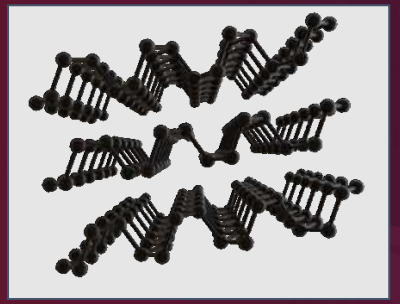
Black Phosphorus

- **α-Black phosphorus:**

  Red phosphorus $\xrightarrow[\text{at 803 K}]{\text{Sealed tube}}$ α-Black phosphorus

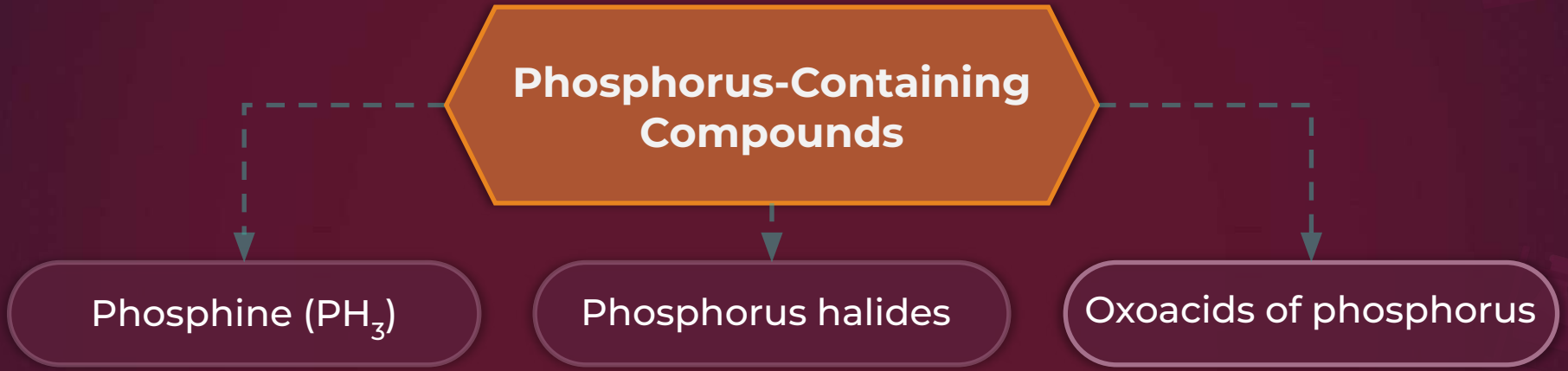
- **β-Black phosphorus:**

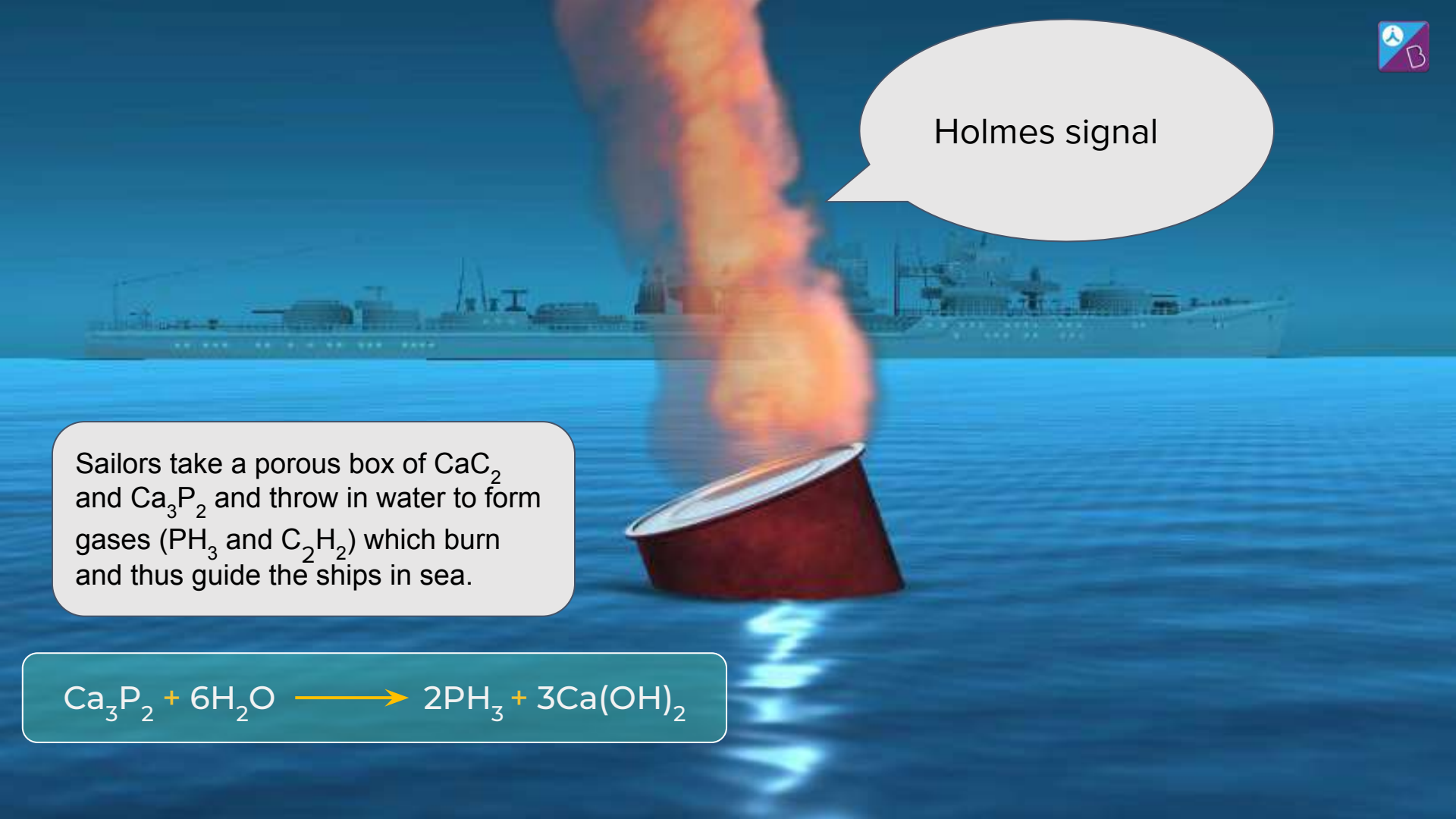
  White phosphorus $\xrightarrow[\text{473 K}]{\text{Under high pressure}}$ β-Black phosphorus



Thermal Stability Order

White phosphorus < Red phosphorus < Black phosphorus


Phosphorus-Containing Compounds
Phosphine (PH_3)
Phosphorus halides
Oxoacids of phosphorus


Holmes signal
Sailors take a porous box of CaC_2 and Ca_3P_2 and throw in water to form gases (PH_3 and C_2H_2) which burn and thus guide the ships in sea.
$Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$

Phosphine

Preparation of Phosphine

- By direct addition of water or dilute HCl to **calcium phosphide.**

$$Ca_3P_2\ (s) + 6H_2O\ (l) \longrightarrow 3Ca(OH)_2\ (aq) + 2PH_3\ (g)$$

$$Ca_3P_2\ (s) + 6HCl\ (aq) \longrightarrow 3CaCl_2\ (aq) + 2PH_3\ (g)$$

- **Laboratory method:** By addition of white phosphorus to sodium hydroxide in an **inert atmosphere.**

Physical Properties of PH_3

1. **Colourless** gas
2. **Rotten fish-like** smell
3. Highly **Poisonous**
4. Explodes in contact with traces of **oxidising agents**
5. It is slightly soluble in water but soluble in **organic solvents.**

Example: HNO_3, Cl_2 and Br_2 vapours

Chemical Properties of Phosphine Gas

1. The solution of PH_3 in water **decomposes** in the presence of **light** giving red phosphorus and H_2.

2. When absorbed in copper sulphate or mercuric chloride solution, the corresponding **phosphides** are obtained.

3. **Weakly basic** and give phosphonium compounds with **HBr/HI** only.

Uses

1. The spontaneous combustion of phosphine is technically used in **Holme's signals.**

2. Phosphine gas is used in **smoke screens**

3. Containers containing **calcium carbide** and **calcium phosphide** are pierced and thrown in the sea when the gases evolved burn serve as a signal.

Phosphorus halides

Preparation of PCl_3

1. Obtained by passing **dry chlorine** over heated white phosphorus

$$P_4\,(s) + 6Cl_2\,(g) \longrightarrow 4PCl_3\,(g)$$

2. Obtained by the action of **thionyl chloride** with white phosphorus

$$P_4(g) + 8\,SOCl_2(l) \longrightarrow 4PCl_3\,(l) + 4SO_2(g) + 2S_2Cl_2(l)$$

Properties of Phosphorus Trichloride

Physical Properties

It is a **colourless oily liquid.**

Chemical Properties

Pyramidal shape and sp^3 hybridised.

On hydrolysis gives ortho phosphorus acid.

Act as reducing agent.

Phosphorus halides

Preparation of PCl_5

1

Reaction of white phosphorus with **excess** of dry chlorine.

$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$

2

Prepared by the action of SO_2Cl_2 on phosphorus.

$$P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$$

Properties of Phosphorus Pentachloride

Physical Properties

PCl_5 is a **yellowish white** powder.

Chemical Properties

In moist air, it hydrolyses to **$POCl_3$** and finally gets converted to **phosphoric acid.**

$$PCl_5\ (g) + H_2O\ (l) \longrightarrow POCl_3\ (g) + 2HCl\ (aq)$$

$$POCl_3\ (aq) + 3H_2O\ (l) \longrightarrow H_3PO_4\ (aq) + 3HCl\ (aq)$$

Structure of Phosphorus Pentachloride

In gaseous and liquid phase, its hybridisation is sp^3d and its shape will be **trigonal bipyramidal (TBP)**.

In solid state, it exists as

$[PCl_4]^+ [PCl_6]^-$.

Tetrahedral **Octahedral**

Oxoacids of Phosphorus

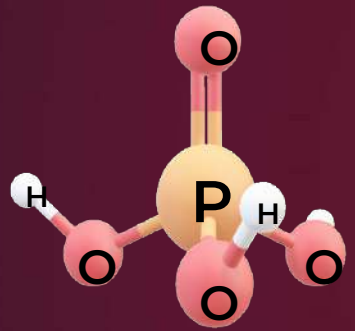
Name	Hypophosphorous acid	Orthophosphorous acid	Pyrophosphorous acid
Formula	H_3PO_2	H_3PO_3	$H_4P_2O_5$
Oxidation Number	+1	+3	+3
Characteristic	One P-OH Two P-H One P=O	Two P-OH One P-H One P=O	Two P-OH Two P-H Two P=O One P-O-P
Preparation	White P_4 + alkali	$P_2O_3 + H_2O$	$PCl_3 + H_3PO_3$

Orthophosphorus Acid

Orthophosphorous acid (or phosphorous acid) on heating **disproportionates** to give orthophosphoric acid (or phosphoric acid) and phosphine.

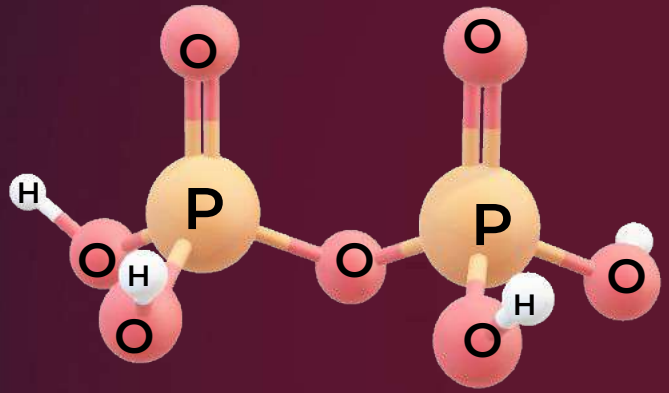
$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

Orthophosphoric Acid



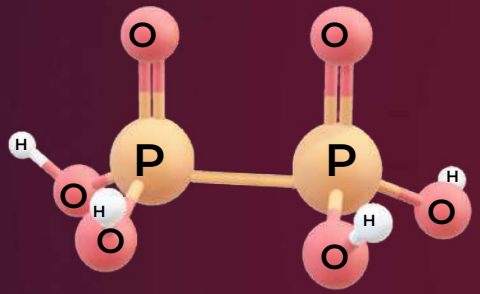
Name	Orthophosphoric Acid
Formula	H_3PO_4
Oxidation	+5
Characteristic	Three P-OH One P=O
Preparation	$P_4O_{10} + H_2O$

Pyrophosphoric Acid



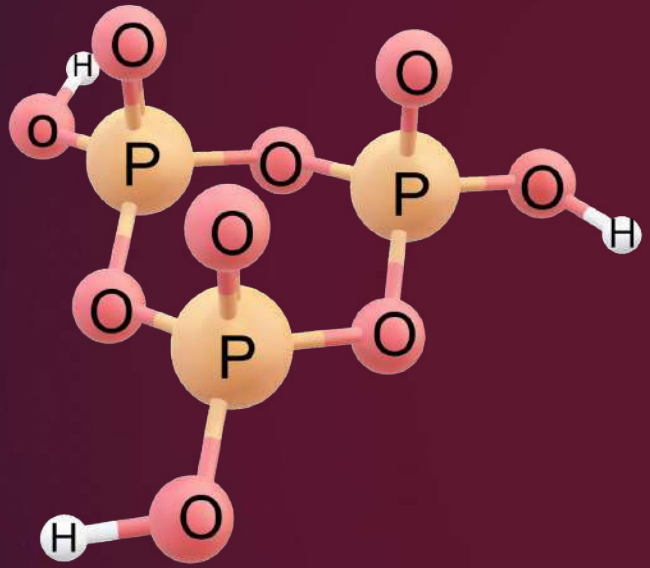
Name	Pyrophosphoric Acid
Formula	$H_4P_2O_7$
Oxidation	+5
Characteristic	Four P-OH Two P=O One P-O-P
Preparation	Heating phosphoric acid

Hypophosphoric Acid



Name	Hypophosphoric acid
Formula	$H_4P_2O_6$
Oxidation	+4
Characteristic	Four P-OH One P-P Two P=O
Preparation	Red P_4 + alkali

Metaphosphoric Acid



Name	Metaphosphoric Acid
Formula	$(HPO_3)_n$
Oxidation	+5
Characteristic	Three P-OH Three P=O Three P-O-P
Preparation	Phosphorus acid + Br_2, heat in a sealed tube

Group 16 Elements

- Oxygen (O_8^{16})
- Sulphur (S_{16}^{32})

→ Non-metals

Known as group of **chalcogens.**

- Selenium
- Tellurium

→ Metalloids

Polonium is **radioactive** and short-lived (half-life 13.8 days).

- Polonium

→ Radioactive metal

Radioactive materials

Occurrence

Oxygen

Most abundant of all elements

Exists in free form as O_2 and makes up **20.9%** by volume and **23%** by weight of atmosphere.

Most of the oxygen is produced by **photosynthesis.**

$$6CO_2 + 6H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2$$

Sulphur

Constitutes **0.034%** by weight of earth's crust and occurs mainly in combined form as ores of sulphides and sulphates (particularly **gypsum**).


Baryte:
$BaSO_4$


Copper Pyrite:
$CuFeS_2$


Zinc Blende:
ZnS

Atomic Properties

- Electronic configuration
- Atomic & ionic radii
- Ionisation enthalpy
- Electron gain enthalpy
- Electronegativity

Electronic Configuration

The elements of group 16 have **six** electrons in the outermost shell.

General valence shell electronic configuration

ns^2np^4

Atomic And Ionic Radii

Down the group, atomic and ionic radii increases due to **increase** in number of shells

Ionisation Enthalpy

Group 15 elements > Group 16 elements

O < S < Se < Te

$ns^2\ np^3$ $ns^2\ np^4$

Group 15 elements have higher ionisation enthalpy because of **extra stable** half-filled p subshell

Electron Gain Enthalpy

Down the group

For O	From S to Po
Due to compact nature, it has less negative electron gain enthalpy than S.	The value again becomes less negative up to polonium.

Electronegativity

Order

O > S > Se > Te > Po

Down the group

Decreases

with increase in atomic size.

Physical Properties

1. Down the group **Metallic character increases** with **increase** in atomic size

2. Down the group **catenation** decreases. But Sulphur has higher catenation ability than Oxygen, due to high interelectronic repulsions in O-O sigma bond.

3. **Boiling point:** O < S < Se < Te > Po

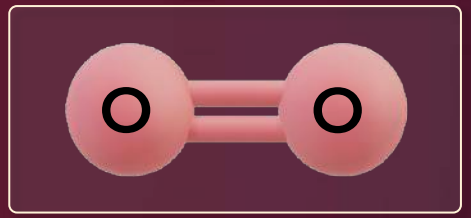
4. **Melting point :** O < S < Se < Te > Po

Physical Properties

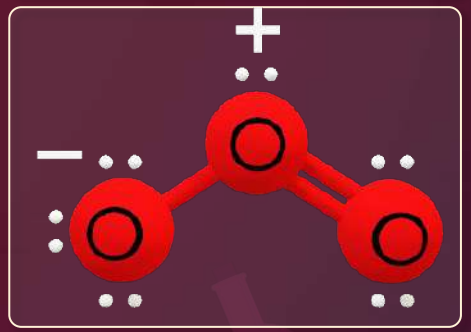
All elements show allotropy.

Oxygen exists in two allotropic forms

- Dioxygen O_2



- Ozone O_3 (unstable and decomposes to O_2)



Allotropes of Sulphur

1. Two common forms are α or rhombic sulphur and β or monoclinic sulphur.

2. Transition temperature is **95.5 ^{0}C**, below which α **form** exists and above which the β **form** exists.

3. A third form known as γ-monoclinic sulphur is also present.

4. All three forms contain **puckered S_8 rings** with a crown conformation.

Rhombic (α-Sulphur)

1. It is **yellow** in colour and its specific gravity is 2.06.
2. Melting point = **385.8 K**
3. It is readily **soluble in CS_2**.
4. Rhombic sulphur crystals are formed on **evaporating** the solution of roll sulphur in CS_2.
5. It is **insoluble in water** but gets dissolved to some extent in benzene, alcohol and ether.

Monoclinic (β-Sulphur)

1. Its melting point is **393 K** and specific gravity is 1.98.

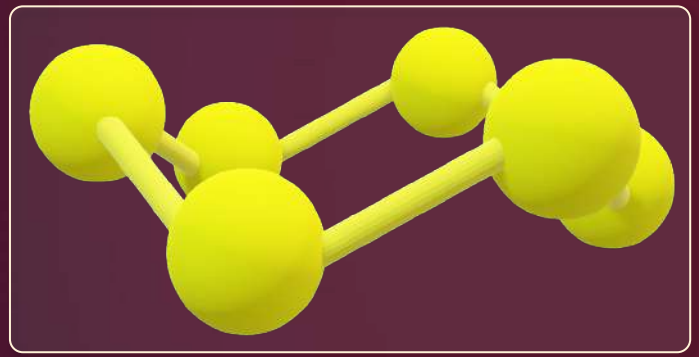
2. It is **soluble in CS_2**.

3. This form of sulphur is prepared by **melting** rhombic sulphur in a dish and cooling it till crust is formed.

Two holes are made in the crust and the remaining liquid is poured out.

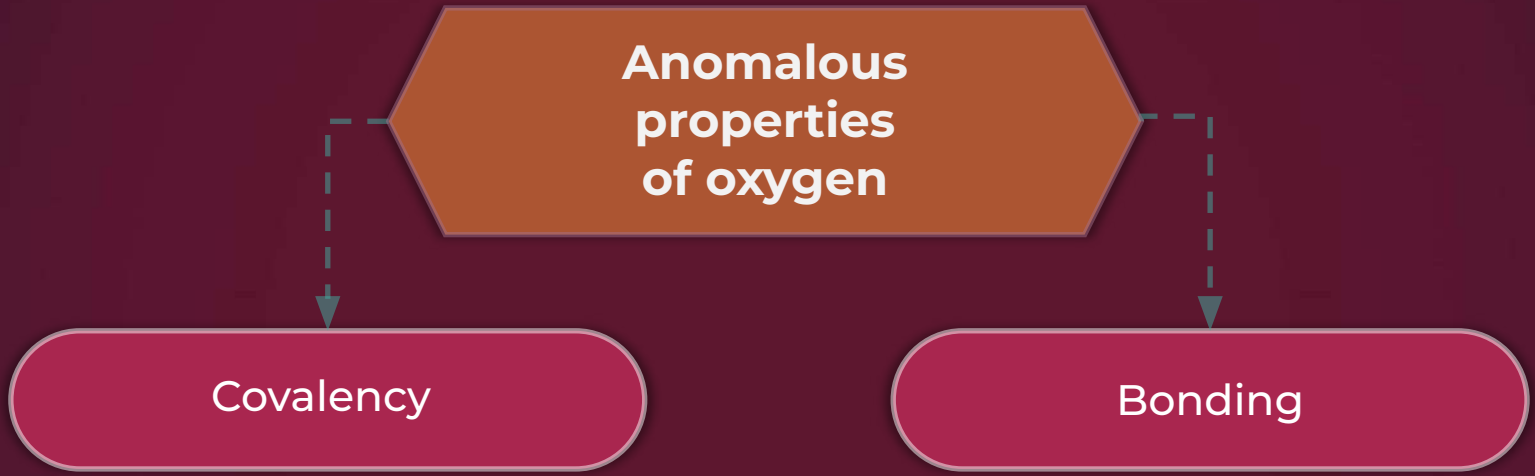
On removing the crust, **colourless, needle-shaped crystals** of β-sulphur are formed.

Allotropes of Sulphur



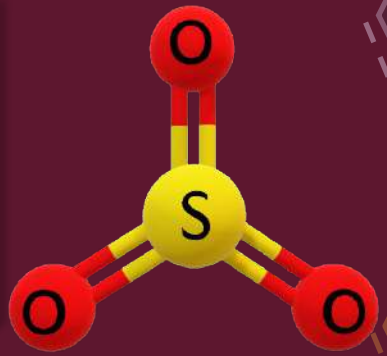
Several other modifications of sulphur containing **6-20** sulphur atoms per ring have been synthesised in the last two decades.

In cyclo-S_6, the ring adopts the **chair form.**


Anomalous properties of oxygen
Covalency
Bonding

Covalency

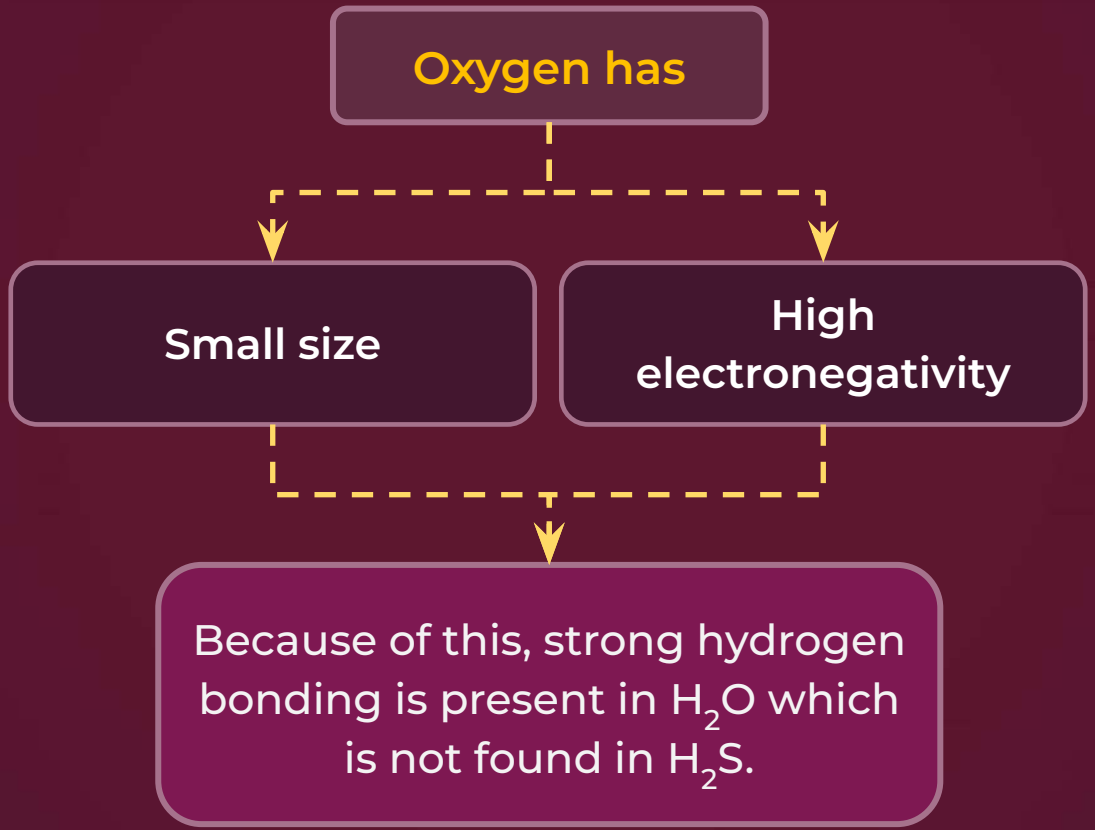
The **absence of d-orbitals** in oxygen **restricts** its covalency to **4** and **rarely increases beyond 2.**



In case of **other elements** of the same group,

The valence shell can be **expanded** and covalency **exceeds four.**

Bonding


Oxygen has
Small size
High electronegativity
Because of this, strong hydrogen bonding is present in H_2O which is not found in H_2S.


General Trends
& Chemical
Properties

Oxidation State

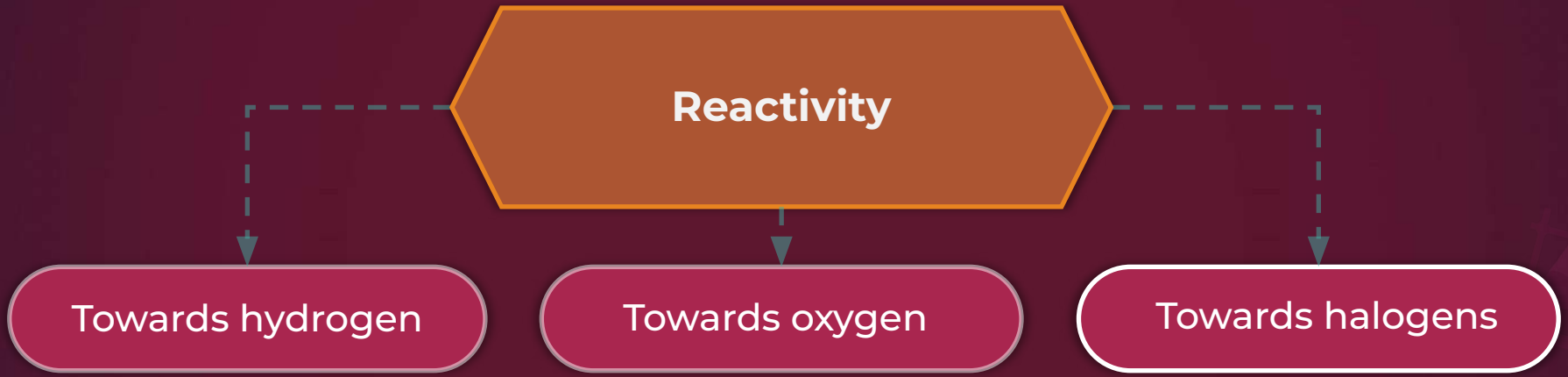
Down the group tendency to exhibit -2 oxidation state **decreases.**

Down the group tendency to exhibit +4 oxidation state increases due to **inert pair effect.**

Down the group tendency to exhibit **+6** oxidation state **decreases.**

The compounds in which these elements are showing **+4** and **+6**, are **predominantly covalent.**

Chemical Properties



Properties of Hydrides

Thermal stability

H_2O > H_2S > H_2Se > H_2Te

Hydrides	$\Delta_{diss}H^0$ of H–E (kJ mol^{-1})
H_2O	463
H_2S	347
H_2Se	276
H_2Te	238

$\Delta_{diss}H^0$: Bond dissociation enthalpy

Properties of Hydrides

Acidity

H_2Te > H_2Se > H_2S > H_2O

Hydrides	K_a Value
H_2O	1.8×10^{-16}
H_2S	1.3×10^{-7}
H_2Se	1.3×10^{-4}
H_2Te	2.3×10^{-3}

K_a: Dissociation constant

Properties of Hydrides

Boiling Point

H_2O > H_2Te > H_2Se > H_2S

Generally,

Boiling point ∝ **Molecular weight**

Down the group → Boiling point ↑

H_2O has high **boiling point** as compared to other hydrides.

Due to hydrogen bond

Properties of Hydrides

Reducing property

All the hydrides **except water** possess reducing property.

This character **increases** from H_2S to H_2Te.

Reactivity Towards Oxygen

All the elements form two types of oxides EO_2 and EO_3.

Down the group, reducing power of dioxide increases.

Trioxides act only as oxidising agents.

Both dioxides and trioxides are acidic in nature.

Reactivity Towards Halogens

These elements react to form three series of halides.

EX_6, EX_4, EX_2

E = Element of group 16,
X = Halogen

Stability

Order of stability of halides

$F^- > Cl^- > Br^- > I^-$

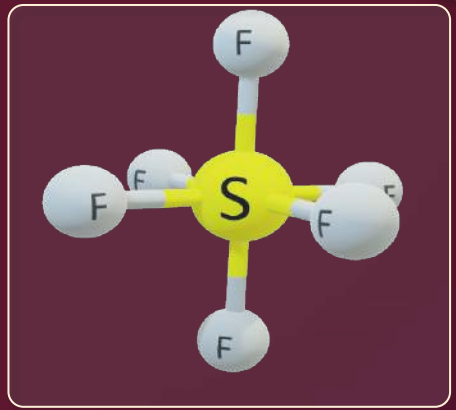
Hexahalides

1. Amongst hexahalides, **hexafluorides** are the only **stable** halides.

2. All hexafluorides are **gaseous** in nature.

3. They have an **octahedral** structure.

Sulphur hexafluoride **(SF_6)** is exceptionally **stable** due to steric reasons.



Sulphur Hexafluoride (SF_6)

Tetrafluoride

Tetrafluorides have sp^3d hybridisation.

↓

Trigonal bipyramidal geometry

↓

One of the **equatorial position** is occupied by a **lone pair** of electrons.

- - - →

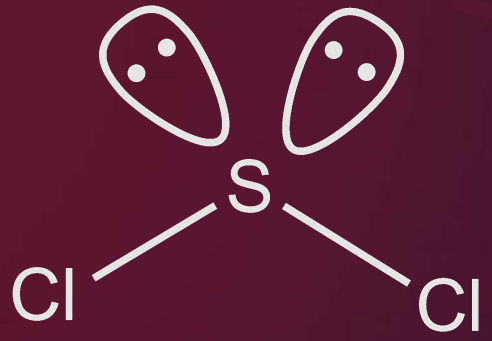
See-saw shape

Dihalides

All elements except **oxygen** form dichlorides and dibromides.

Dihalides formed have sp^3 hybridisation.

Tetrahedral geometry



Monohalides

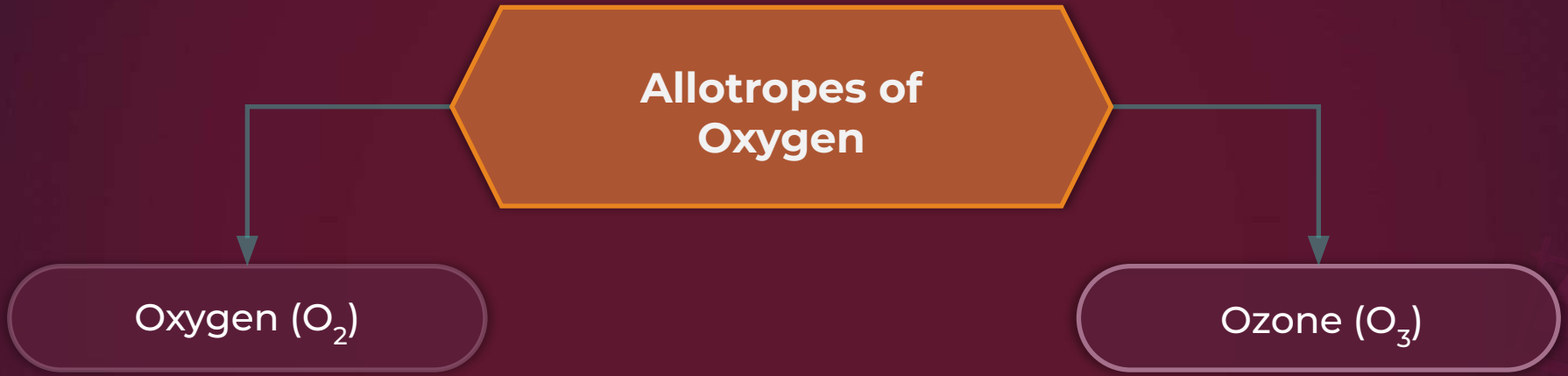
The well-known monohalides are **dimeric** in nature.

These dimeric halides undergo **disproportionation**

$$2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se$$

Examples

S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2, and Se_2Br_2


Allotropes of Oxygen
Oxygen (O_2)
Ozone (O_3)

Preparation of Oxygen Gas

1. Dioxygen is produced industrially by **fractional distillation** of air.

2. **Electrolysis of water** leads to the release of **hydrogen** at the **cathode** and **oxygen** at the **anode.**

$$2KClO_3 \xrightarrow[MnO_2]{150°C} 2KCl + 3O_2 + \text{traces of } Cl_2 \text{ or } ClO_2$$

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

3. **Metal oxides** on decomposition gives **Oxygen.**

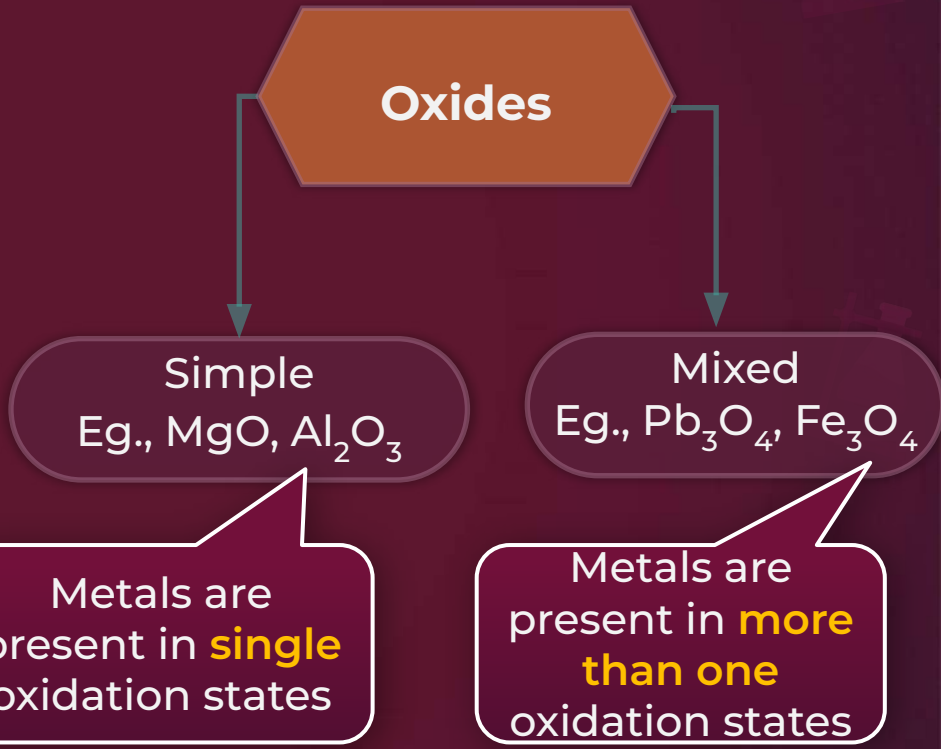
Physical Properties

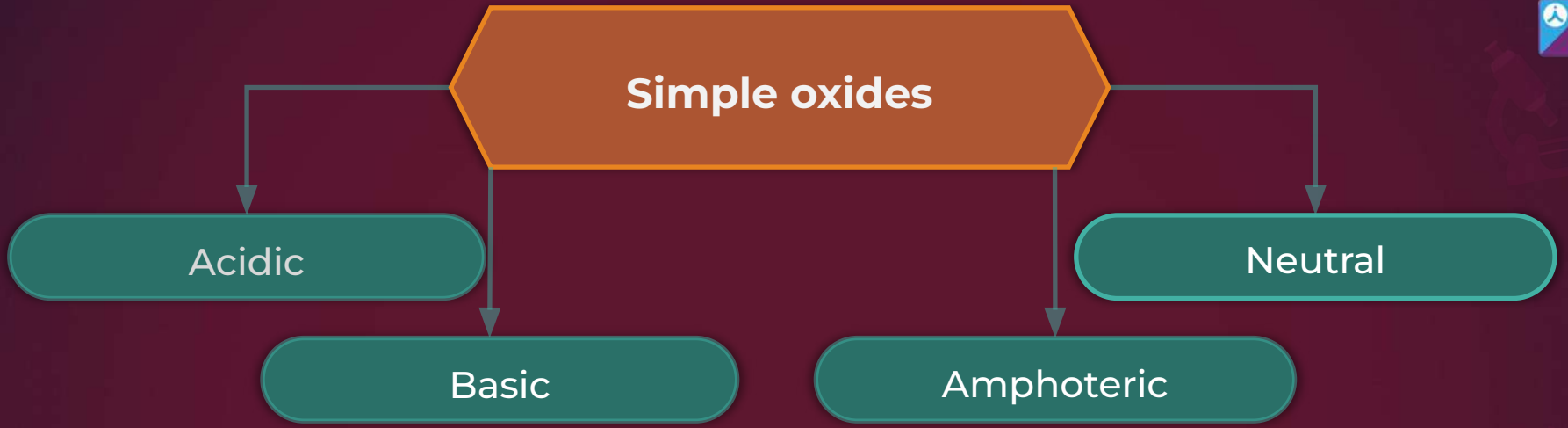
1. Pale blue liquid and a colourless gas
2. Odourless gas
3. Strong supporter of combustion
4. Paramagnetic in nature

Oxides

Oxygen reacts with most of the elements of the periodic table to form **oxides.**

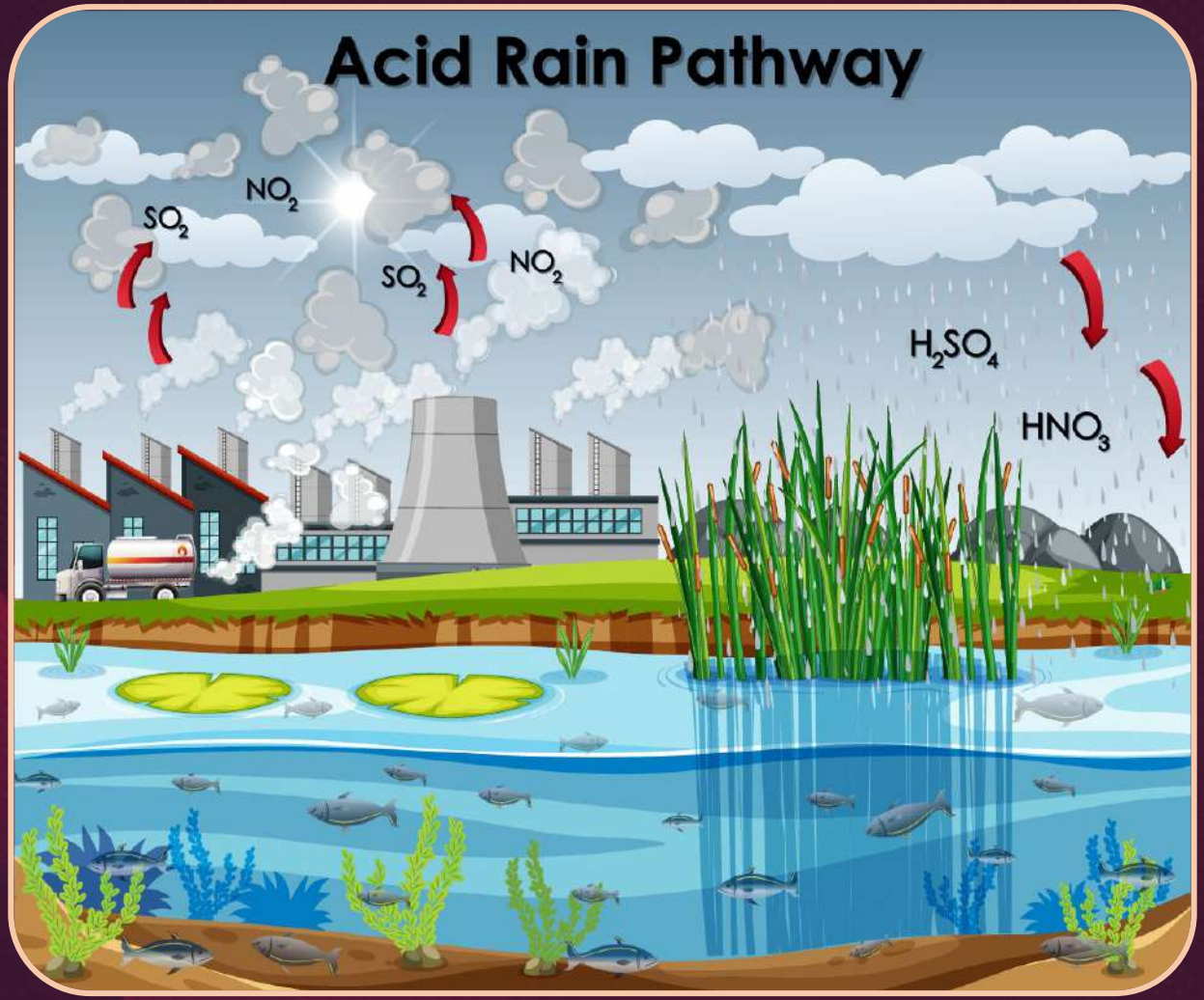
In many cases one element forms **two or more oxides.** The oxides vary widely in their **nature and properties.**





Acidic oxides

1. An oxide that combines with water to give an **acid.**
2. Non-metallic oxides are generally **acidic in nature.**
3. Example: SO_2, Cl_2O_7, CO_2, N_2O_5


Acid Rain Pathway
NO_2
SO_2
SO_2
NO_2
H_2SO_4
HNO_3

Basic Oxides

Oxides that give a **base** on reaction with water.

In general, metallic oxides are basic in nature.

Example

Na_2O, CaO, BaO

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Amphoteric Oxides

Some metallic oxides exhibit a dual behaviour. They show characteristics of both acidic as well as basic oxides.
Example: Al_2O_3

$$Al_2O_3(s) + 6HCl(aq) + 9H_2O(l) \longrightarrow 2[Al(H_2O)_6]^{3+}(aq) + 6Cl^-(aq)$$

$$Al_2O_3(s) + 6NaOH(aq) + 3H_2O(l) \longrightarrow 2Na_3[Al(OH)_6](aq)$$

Neutral Oxides

Oxides that are **neither acidic nor basic.**

Such oxides are known as **neutral oxides.**

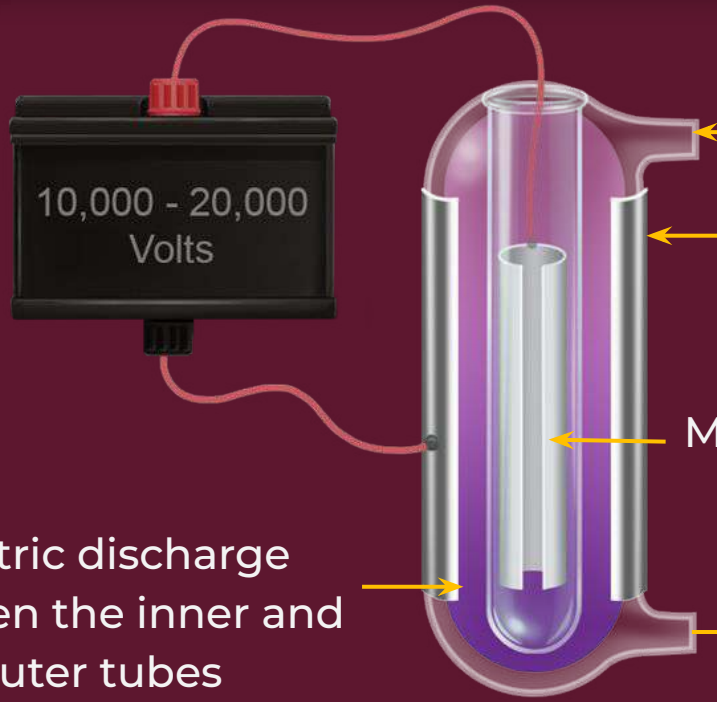
E.g., CO, NO, and N_2O

Ozone

Silent **electrical discharge** is used in the preparation of ozone to prevent its **decomposition.**

$$3O_2 \longrightarrow 2O_3;\ \Delta H^0\ (298\ K) = +142\ kJ\ mol^{-1}$$

Preparation of Ozone



Dry O_2 gas

Metal foil outside of the outer glass tube

Metal foil inside of the inner glass tube

Electric discharge between the inner and outer tubes

O_3 in O_2

Preparation of Ozone

Silent electrical discharge is used in the preparation of ozone to prevent its **decomposition.**

Mixture obtained contains **5–10% ozone** by volume, and this mixture is called **ozonised oxygen**.

Higher concentration or pure O_3 can be obtained by **fractional liquefaction** of the mixture.

Physical Properties of Ozone

1

Gas – dark blue
Liquid – blue
Solid – violet

2

It has a **characteristic smell** and is **toxic** in high concentrations (> 100 ppm)

Chemical Properties of Ozone

O_3 is thermodynamically unstable with respect to O_2

Exothermic reaction

$$O_3 \longrightarrow O_2 + O$$

ΔG = -ve

Large negative

High conc. of ozone can be **dangerously explosive**.

Chemical Properties of Ozone

Oxidising agent

Ozone acts as a powerful oxidising agent due to the ease with which it liberates the atoms of **nascent oxygen.**

$$O_3 \longrightarrow O_2 + [O]$$

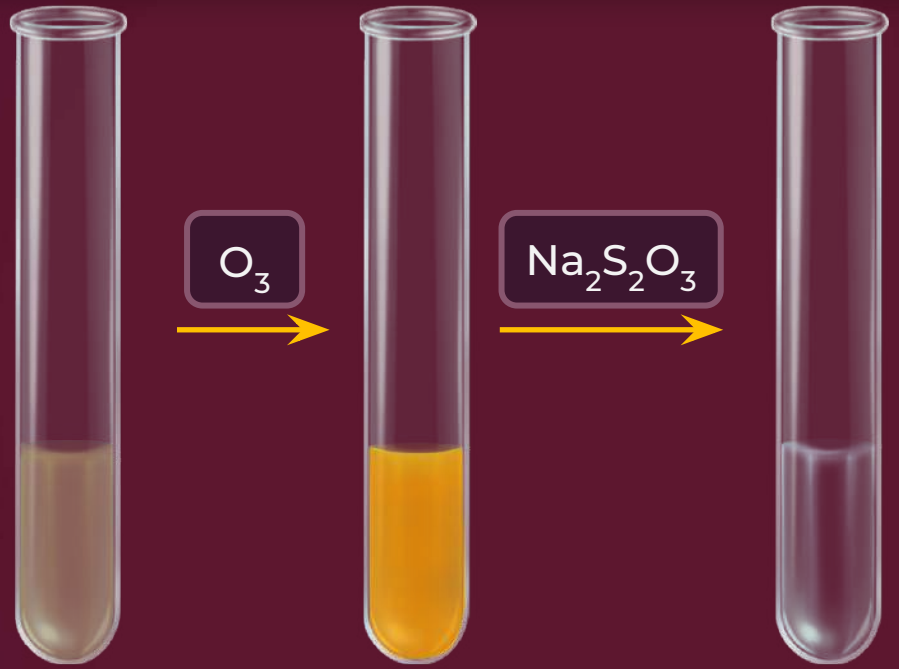
Ozone

Buffered with a borate buffer (pH = 9.2)

When ozone reacts with an **excess of KI** solution

Iodine is liberated, which can be titrated against a **standard solution of $Na_2S_2O_3$**

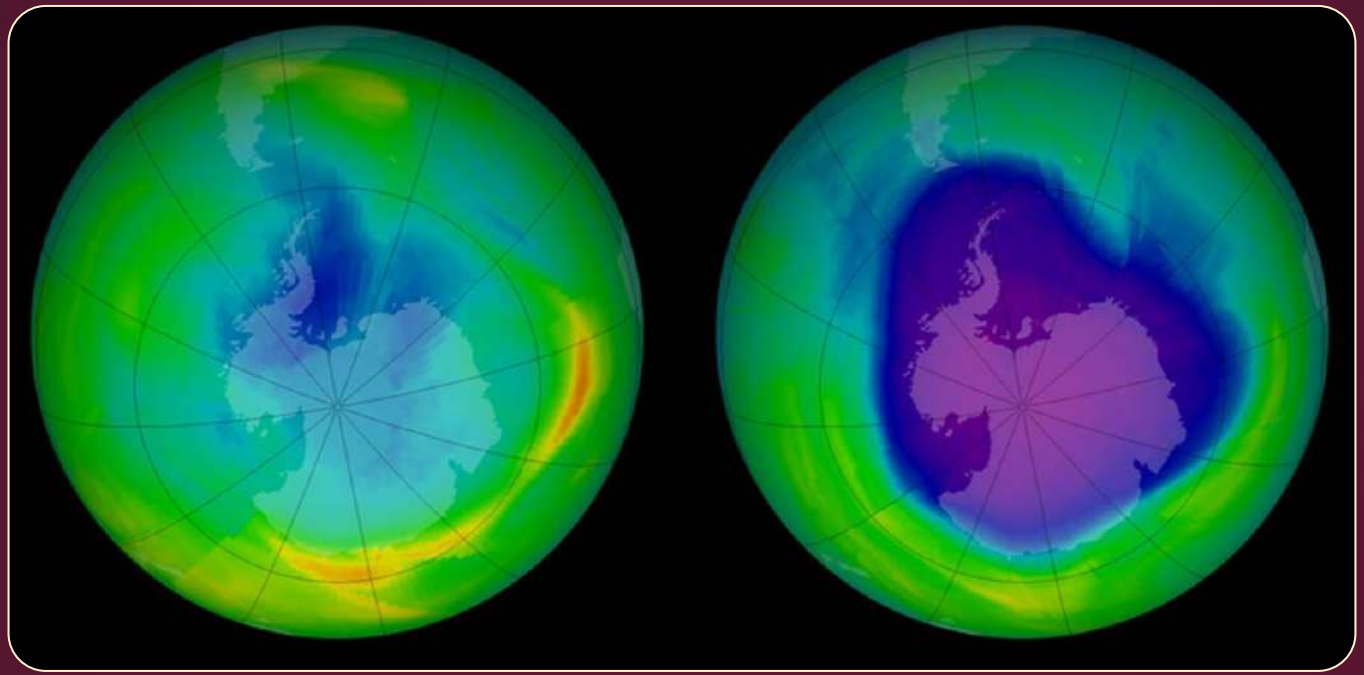
Estimation of Ozone



KI Solution

I_2 Solution

I_2 liberated is estimated with hypo solution



Ozone Hole

Ozone depletion

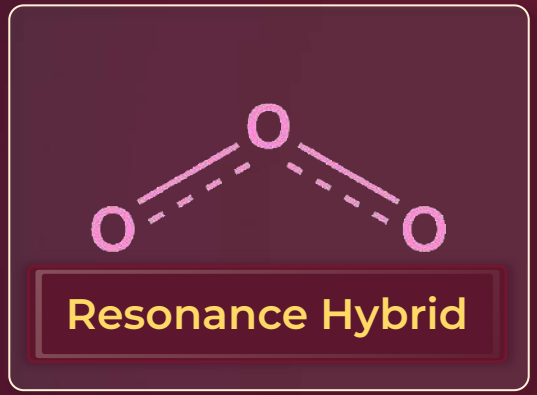
Particularly nitric oxide

Experimentally, nitrogen oxide combine very rapidly with O_3

$$NO\ (g) + O_3\ (g) \longrightarrow NO_2\ (g) + O_2\ (g)$$

There is a possibility that **nitrogen oxides** emitted from the exhaust systems of **supersonic jet aeroplanes** might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

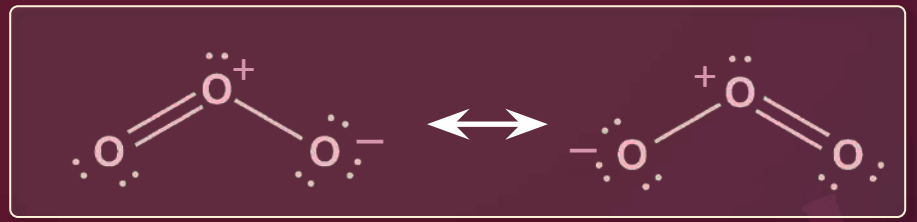
Ozone Structure



128 pm

The two O–O bond lengths are **identical**

It is a **resonance hybrid** of the two possible resonating structures.



Uses of Ozone

- Sterilising
- Disinfectant
- Bleaching agent
- Protects us from harmful UV radiation of sun

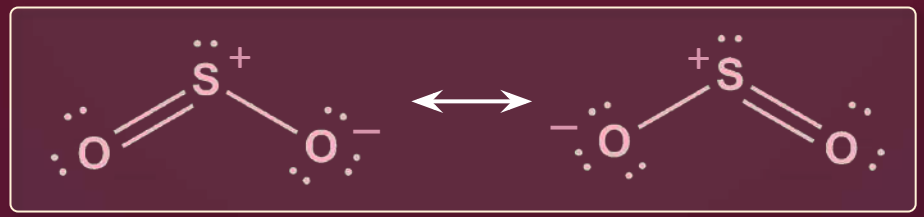
Sulphur Dioxide (SO_2)

Resonance hybrid

Both the bonds are **equivalent**

Molecule of SO_2 is **Bent or V-shaped.**

It is a resonance hybrid of the two canonical forms



Preparation of Sulphur Dioxide

1. **Little amount** of sulphur dioxide can be prepared by direct heating of **sulphur** in **air or oxygen**.

$$S + O_2 \text{ or air} \xrightarrow{\text{Burn}} SO_2$$

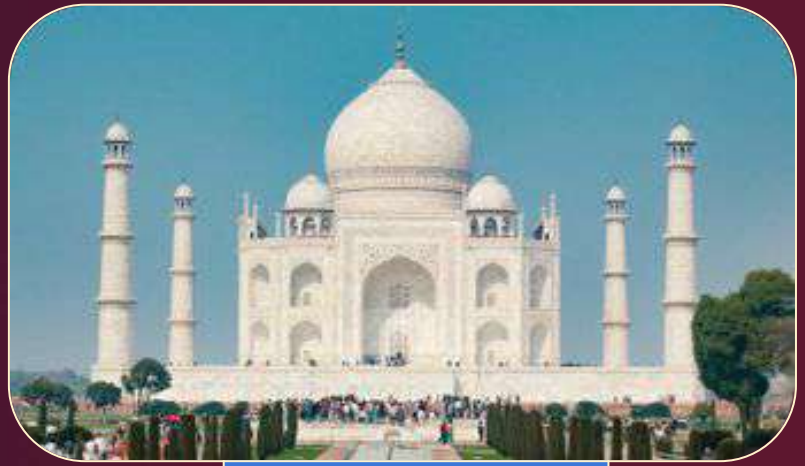
2. Sulphur dioxide can also be prepared by treating **sulphite** with **dilute sulphuric acid**.

$$SO_3^{2-}(aq) + 2H^+(aq) \longrightarrow H_2O(l) + SO_2(g)$$

Physical Properties of SO_2

Colourless gas with a burning sulphur smell

Highly **soluble** in water



Then

Now

Chemical Properties of Sulphur Dioxide

1. Sulphur dioxide dissolves in water to form sulphurous acid (H_2SO_3)

2. It reacts with NaOH to form sodium sulphite (Na_2SO_3), then reacts with more sulphur dioxide to form sodium hydrogen sulphite ($NaHSO_3$)

3. It is a powerful reducing agent.

4. It decolourise the solution of potassium permanganate $KMnO_4$ (can be used a test for SO_2 gas).

Uses of SO_2

In refining sugar

In refining petroleum

As an anti-chlor

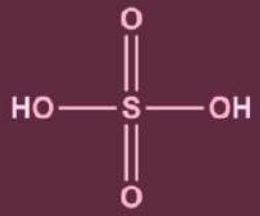
Oxoacids of Sulphur

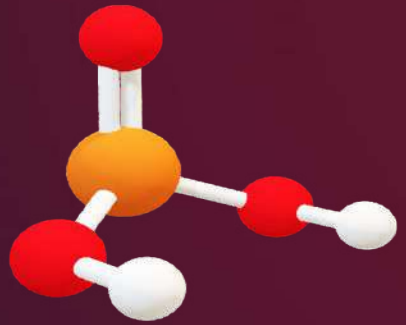
Sulphur forms a number of oxoacids such as H_2SO_3, H_2SO_4, $H_2S_2O_7$, $H_2S_2O_8$

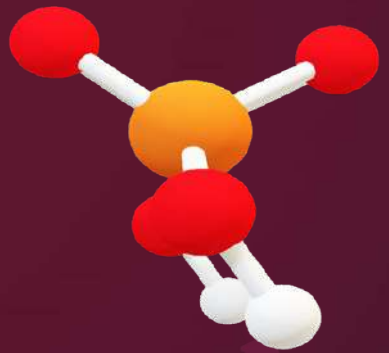
Some of these acids are **unstable** and cannot be isolated.

Oxoacids of Sulphur

Oxidation state	+4
Structure	

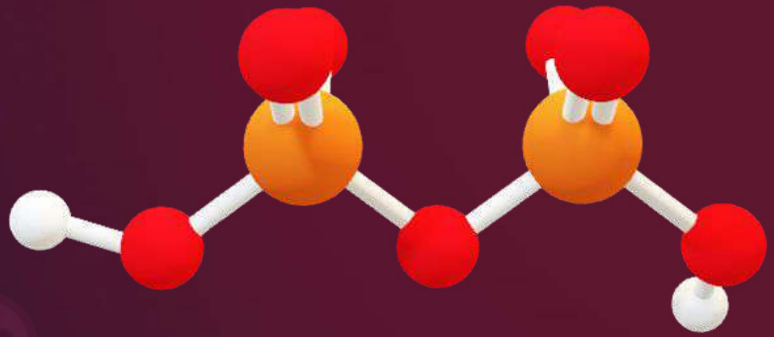
Oxidation state	+6
Structure	



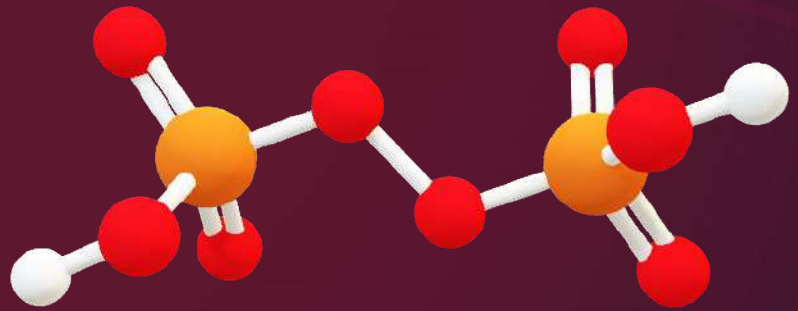


Oxoacids of Sulphur

Oxidation state	+6, +6
Structure	



Oxidation state	+6, +6
Structure	



Sulphuric Acid

Preparation:

Sulphuric acid is manufactured by the contact process.

Sulphuric acid obtained by contact process is 96–98% pure.

Contact Process

1. Sulphur or sulphide ores are burnt in air to generate SO_2

$$S + O_2\,(g) \longrightarrow SO_2\,(g)$$

SO_2 produced is purified by removing dust and other impurities such as arsenic compounds

Contact Process

2 Conversion of SO_2 to SO_3 by reaction with oxygen in the presence of a catalyst (V_2O_5)

$$2SO_2(g) + O_2(g) \overset{V_2O_5}{\rightleftharpoons} 2SO_3(g)$$

$$\Delta_r H = -196.6 \text{ kJ mol}^{-1}$$

Reaction is exothermic, reversible

Low temperature (not too low) and high pressure are the favourable conditions for maximum yield.

Contact Process

3 Absorption of SO_2 in H_2SO_4 to give oleum ($H_2S_2O_7$)

↓

Dilution of oleum with water gives **H_2SO_4** of the desired concentration

Properties of H_2SO_4

Physical properties

1. Colourless, dense, oily liquid
2. Dissolves in water with the evolution of a large quantity of heat

Chemical Properties

Oxidising agent in aqueous solution

Characteristics of sulphuric acid

- **Strong acidic** character
- **Strong affinity** for water

Chemical Properties of H_2SO_4

Sulphuric acid ionises in **two steps**

$$H_2SO_4\,(aq) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + HSO_4^-\,(aq)$$

K_{a_1} = very large ($K_{a_1} > 10$)

$$HSO_4^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + SO_4^{2-}\,(aq)$$

$K_{a_2} = 1.2 \times 10^{-2}$

Chemical Properties of H_2SO_4

Larger value of K_{a_1} ($Ka_1 > 10$) means that H_2SO_4 is largely dissociated into H^+ and HSO_4^-

Greater dissociation constant (K_a)

Stronger is the acid

Chemical Properties of H_2SO_4

Sulphuric acid forms two series of salts

- Normal sulphates
  - Example: Sodium sulphate and copper sulphate
- Acid sulphate
  - Example: Sodium hydrogen sulphate

Concentrated H_2SO_4 is a **strong dehydrating agent**

It removes water from **organic compound**

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

Uses of H_2SO_4

Preparation of SO_3

1

$$6H_2SO_4 + P_4O_{10} \longrightarrow 6SO_3 + 4H_3PO_4$$

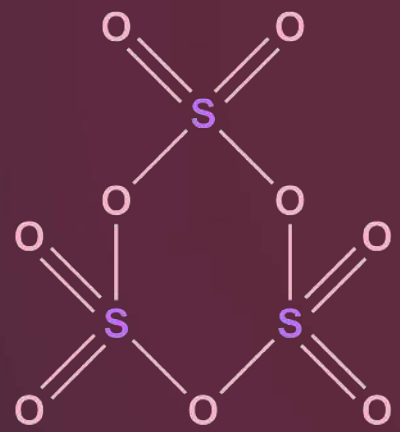
2

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$$

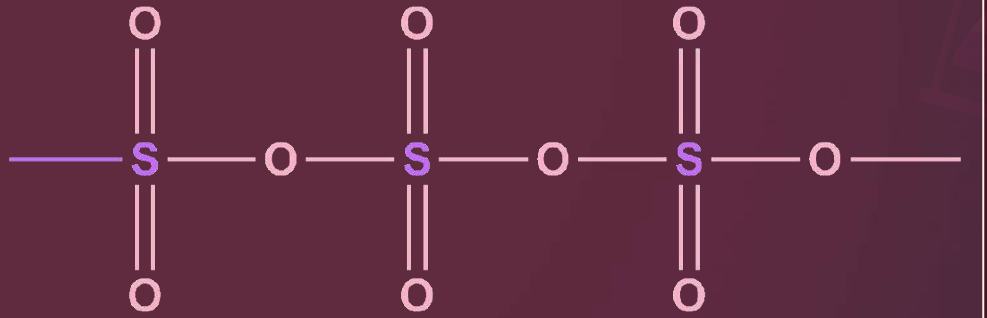
Physical Properties of SO_3

1

SO_3 exists in three allotropic forms:
γ-SO_3, α-SO_3/β-SO_3



γ-SO_3



α-SO_3 or β-SO_3

Physical Properties of SO_3

2. Colourless to white crystalline solid

3. Soluble in water.

4. Odourless

Chemical Properties of SO_3

1. SO_3 is a **powerful oxidising agent**, especially when hot.

$$5SO_3 + 2P \xrightarrow{\Delta} 5SO_2 + P_2O_5$$

$$SO_3 + 2HBr \xrightarrow{\Delta} H_2O + Br_2 + SO_2$$

2. **Acidic nature:** It dissolves in water to form sulphuric acid.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7 \text{ (Oleum)}$$

Preparation of H_2S

It is prepared in **Kipp's** apparatus.

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$

Preparation of **pure H_2S gas**.

$$Sb_2S_3\ (pure) + 6HCl\ (pure) \longrightarrow 2SbCl_3 + 3H_2S$$

Physical Properties of H_2S

1. Colourless gas with rotten egg smell

2. **Moderately soluble** in water but solubility decreases with increasing temperature.

Chemical Properties of H_2S

1

H_2S acts as a **strong reducing agent**.

$$H_2S + X_2 \longrightarrow 2HX + S_2$$

X = F, Cl, Br, I

$$H_2S + 2O_3 \longrightarrow H_2SO_4 + O_2$$

Chemical Properties of H_2S

2

It also reduces MnO_4^- to Mn^{2+},
H_2SO_4 to SO_2 and $K_2Cr_2O_7$ to Cr^{3+}
(acidic medium)

$$5H_2S + 2KMnO_4 + 3H_2SO_4 \longrightarrow 5S + 2MnSO_4 + K_2SO_4 + 8H_2O$$

$$H_2S + H_2SO_4 \longrightarrow S + SO_2 + 2H_2O$$

$$K_2Cr_2O_7 + H_2S + H_2SO_4 \longrightarrow S + K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

Chemical Properties of H_2S

3

It reduces MnO_4^- to MnO_2 (alkaline medium)

$$H_2S + MnO_4^- \longrightarrow S + MnO_2$$

4

Acidic nature

Its aqueous solution acts as a weak dibasic acid according to following reaction:

$$H_2S \rightleftharpoons HS^- + H^+ \rightleftharpoons S^{2-} + 2H^+$$

Chemical Properties of H_2S

Therefore, it forms two series of salts when reacted with a base as given below

$$NaOH + H_2S \longrightarrow NaSH + H_2O$$

Sodium bisulphide

$$2NaOH + H_2S \longrightarrow Na_2S + 2H_2O$$

Sodium sulphide

Preparation of $Na_2S_2O_3.5H_2O$

$$Na_2SO_3 + S \xrightarrow[\text{absence of air}]{\text{Boiled in}} Na_2S_2O_3$$

$$6NaOH + 4s \longrightarrow Na_2S_2O_3 + 2Na_2S + H_2O$$

Properties of $Na_2S_2O_3.5H_2O$

Physical properties

It is a **colourless crystalline substance** which is soluble in water. On heating the water of crystallisation is lost.

Chemical properties

As **antichlor**: It removes the chlorine from the surface of the fibres.

$$Na_2S_2O_3 + 2Cl_2 + 5H_2O \xrightarrow{V_2O_5} 2NaHSO_4 + HCl$$

Chemical Properties of $Na_2S_2O_3.5H_2O$

2

Reducing agent

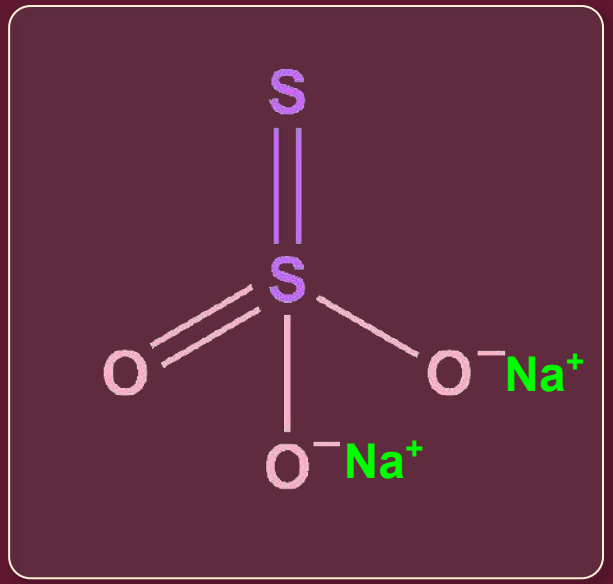
$$I^-_3 + 2Na_2S_2O_3 \longrightarrow 3I^- + Na_2S_4O_6 + 2Na^+$$

3

Heating effect

$$4Na_2S_2O_3.5H_2O \xrightarrow[-H_2O\ (All)]{215\ ^\circ C} 4Na_2S_2O_3 \xrightarrow{220\ ^\circ C} 3Na_2SO_4 + Na_2S_5$$

Structure of $Na_2S_2O_3.5H_2O$



F ree

Cl asses

Br ing

I nfinite

At tendance

Group 17 Elements

These are collectively known as the **halogens.**

Greek: halo
Meaning: salt

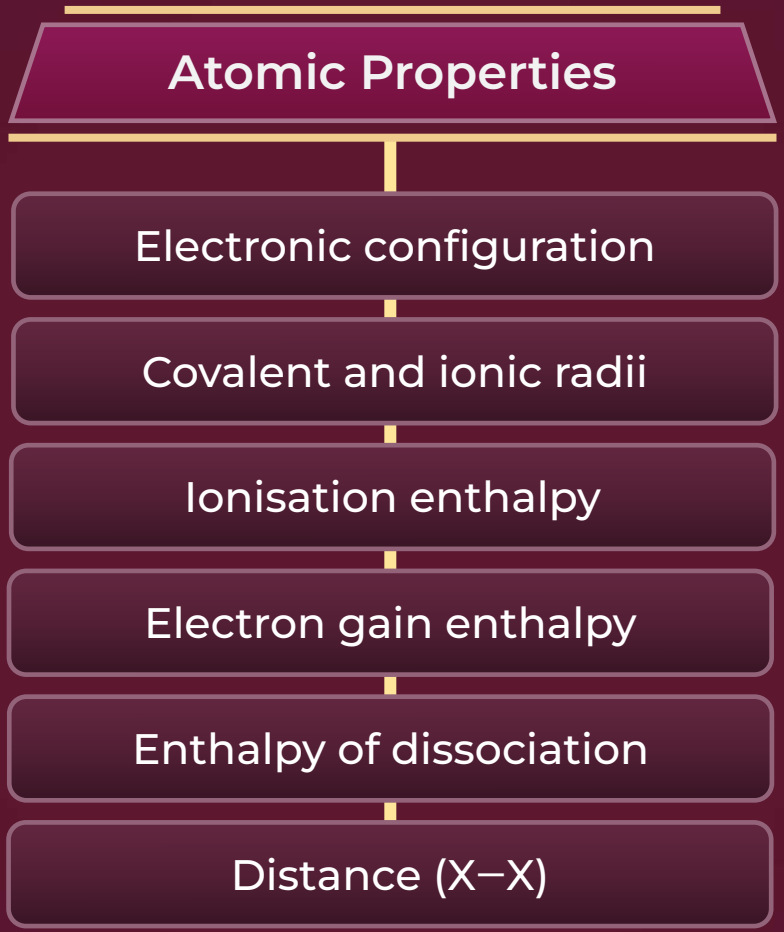
Greek: genes
Meaning: born

Salt producers

Group 17 Elements

- Occurrence
- Atomic properties
- Physical properties
- Chemical properties

Element	Source
F	• Main Source: **Fluorspar** (CaF_2) or **fluorite** • Another Source: **Fluorapatite** $[3Ca_3(PO_4)_2.CaF_2]$ **Cryolite**: Na_3AlF_6
Cl	Most abundant compound of Cl: NaCl (Sea water) Carnallite: $KCl.MgCl_2.6H_2O$
Br	Bromides occur in sea water and brine lakes.
I	• Iodides occur in low concentration in sea water. • Better source: Natural brines


Atomic Properties
Electronic configuration
Covalent and ionic radii
Ionisation enthalpy
Electron gain enthalpy
Enthalpy of dissociation
Distance (X–X)

Atomic Properties

Electronic configuration

General valence shell electronic configuration: ns^2np^5

Element	Electronic configuration
F	$[He]2s^22p^5$
Cl	$[Ne]3s^23p^5$
Br	$[Ar]3d^{10}4s^24p^5$
I	$[Kr]4d^{10}5s^25p^5$

Atomic Properties

Covalent and ionic radii

F < Cl < Br < I

Down the group the number of shells **increase.**

Element	Covalent radii (in pm)	Ionic radii (in pm)
F	64	133
Cl	99	184
Br	114	196
I	133	220

Atomic Properties

Ionisation enthalpy

F > Cl > Br > I

Due to **decrease** in size, removing electrons demands higher energy.

Element	Ionisation enthalpy (in kJ/mol)
F	1680
Cl	1256
Br	1142
I	1008

Atomic and Physical Properties

Electron gain enthalpy

Cl > F > Br > I

Electron gain enthalpy (in kJ/mol)	-349	-333	-325	-296

Maximum negative electron gain enthalpy in the corresponding period

Atomic and Physical Properties

Electron gain enthalpy

Due to small size of fluorine atom

There are **strong interelectronic repulsions** in the relatively **small 2p** orbitals of fluorine.

Thus, the incoming electron does not experience much attraction.

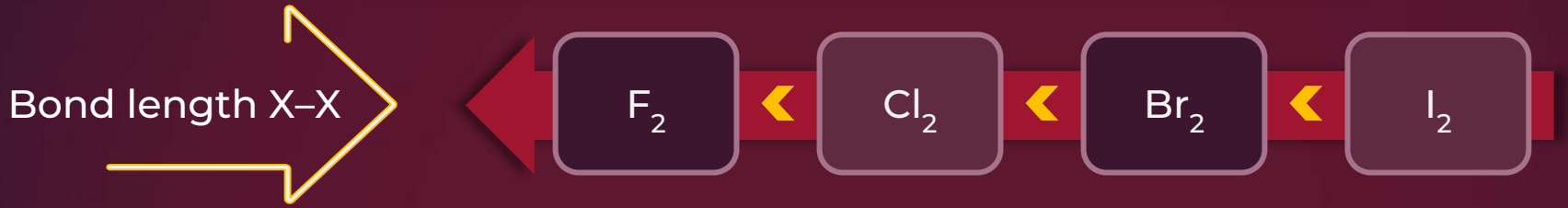
Atomic and Physical Properties

Enthalpy of dissociation (X_2)

Cl–Cl > Br– Br > F–F > I–I

Compound	Enthalpy of dissociation (in kJ/mol)
F–F	158.8
Cl–Cl	242.6
Br–Br	192.8
I–I	151.1

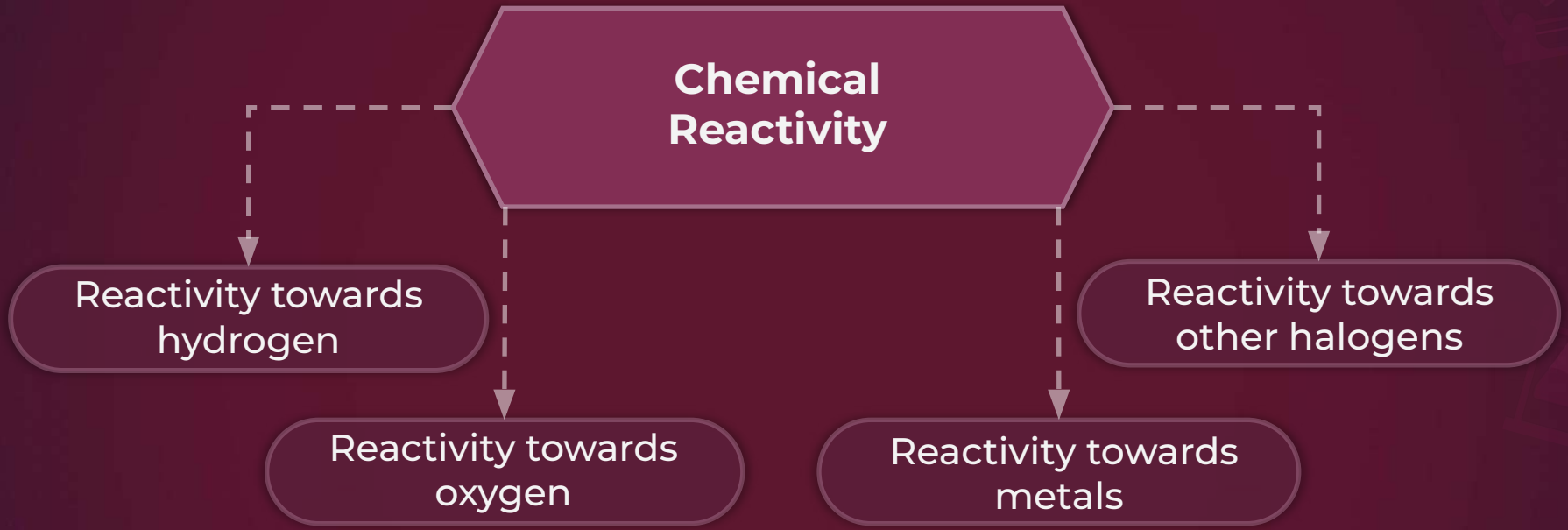
Atomic and Physical Properties



Compound	Distance (in pm)
F_2	143
Cl_2	199
Br_2	229
I_2	266

Physical Properties of Group 17 Elements

- All halogens exist as **diatomic** (X_2) molecule.
- Boiling and melting point order: $F_2 < Cl_2 < Br_2 < I_2$
- Hydration energy order: $F^- > Cl^- > Br^- > I^-$
- Fluorine is a pale green-yellow gas, chlorine is greenish-yellow gas, bromine is reddish brown liquid and iodine is dark violet solid.
- Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water.


Chemical Reactivity
Reactivity towards hydrogen
Reactivity towards oxygen
Reactivity towards metals
Reactivity towards other halogens

Reactivity Towards Hydrogen

$X_2 + H_2 \longrightarrow 2HX$

Where
X = F, Cl, Br, I

Hydrogen halides

Down the group

Reactivity towards H_2 ↓

F_2 reacts violently, whereas I_2 is slow at room temperature.

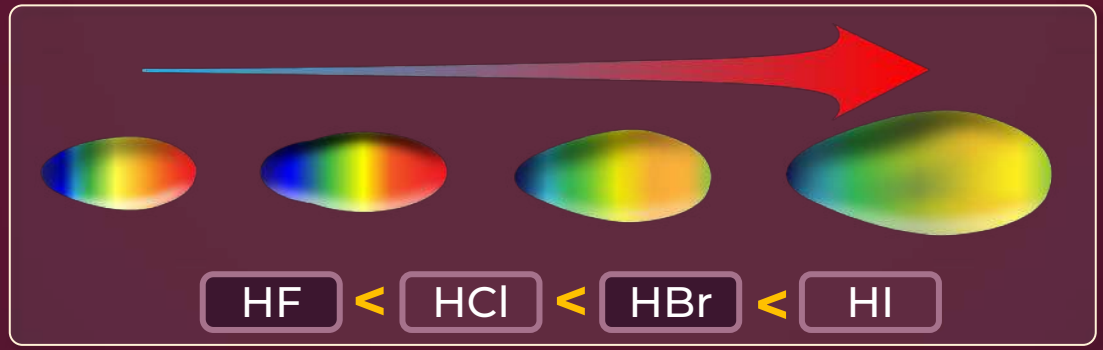
Hydrogen Halides

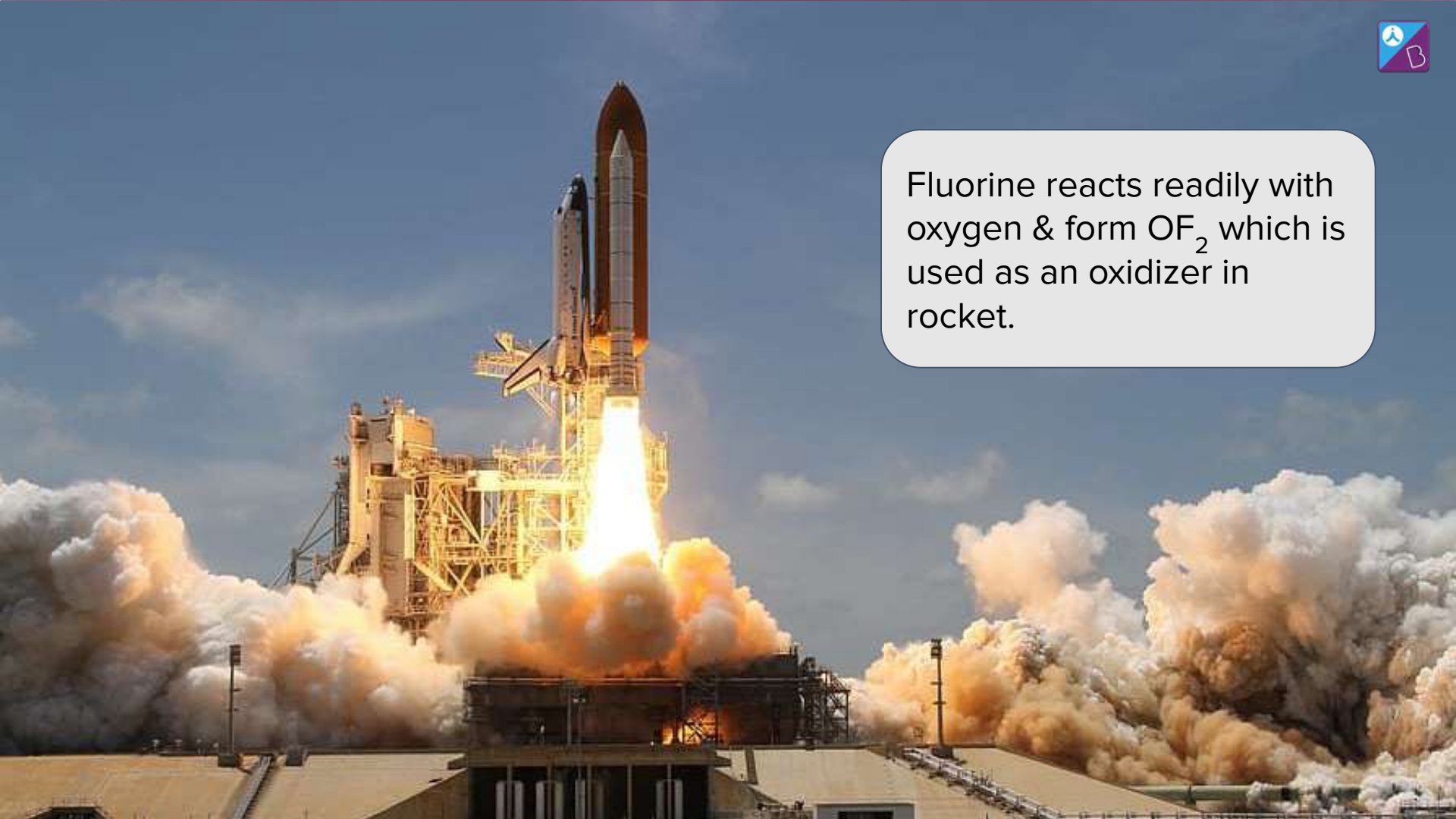
Stability

HF	>	HCl	>	HBr	>	HI
574		432		363		295

$\Delta_{diss}H$ (kJ/mol)

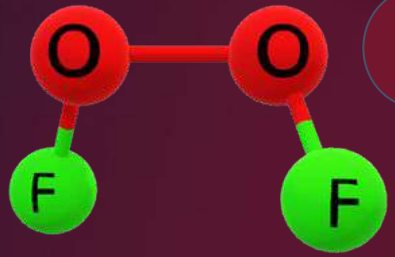
Acidic Strength





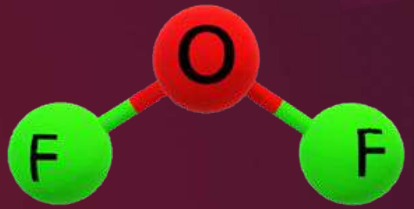
Fluorine reacts readily with oxygen & form OF_2 which is used as an oxidizer in rocket.

Oxygen Fluorides



1. Fluorine forms two oxides, OF_2 and O_2F_2.

Only OF_2 is thermally stable at 298 K.



2. These oxides are essentially **oxygen fluorides** because of the **higher electronegativity** of **fluorine** than oxygen. Both are **strong fluorinating agents**.

Halogen Oxides

3

Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens vary from +1 to +7.

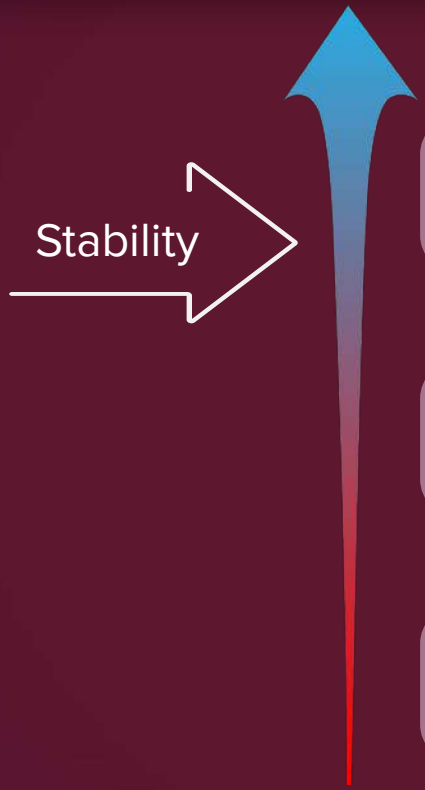
Higher oxides of halogens tend to be more stable than the lower ones.

4

Considering kinetic and thermodynamic factors, stability order of oxides formed by halogens follow the order:

Br < Cl < I

Stability of Halogen Oxides



Oxides of **iodine**

Due to greater **polarisability of I–O bond**

Oxides of **chlorine**

Cl–O multiple bond formation due to availability of d–orbitals

Oxides of **bromine**

Chlorine Oxides

Cl_2O, ClO_2, Cl_2O_6, and Cl_2O_7

Highly reactive oxidising agents and tend to **explode**.

ClO_2 is used as a **bleaching agent** for paper pulp and textiles and in water treatment.

Reactivity Towards Metal

Halogens react with metals to form **metal halides**.

Ionic character

General reaction

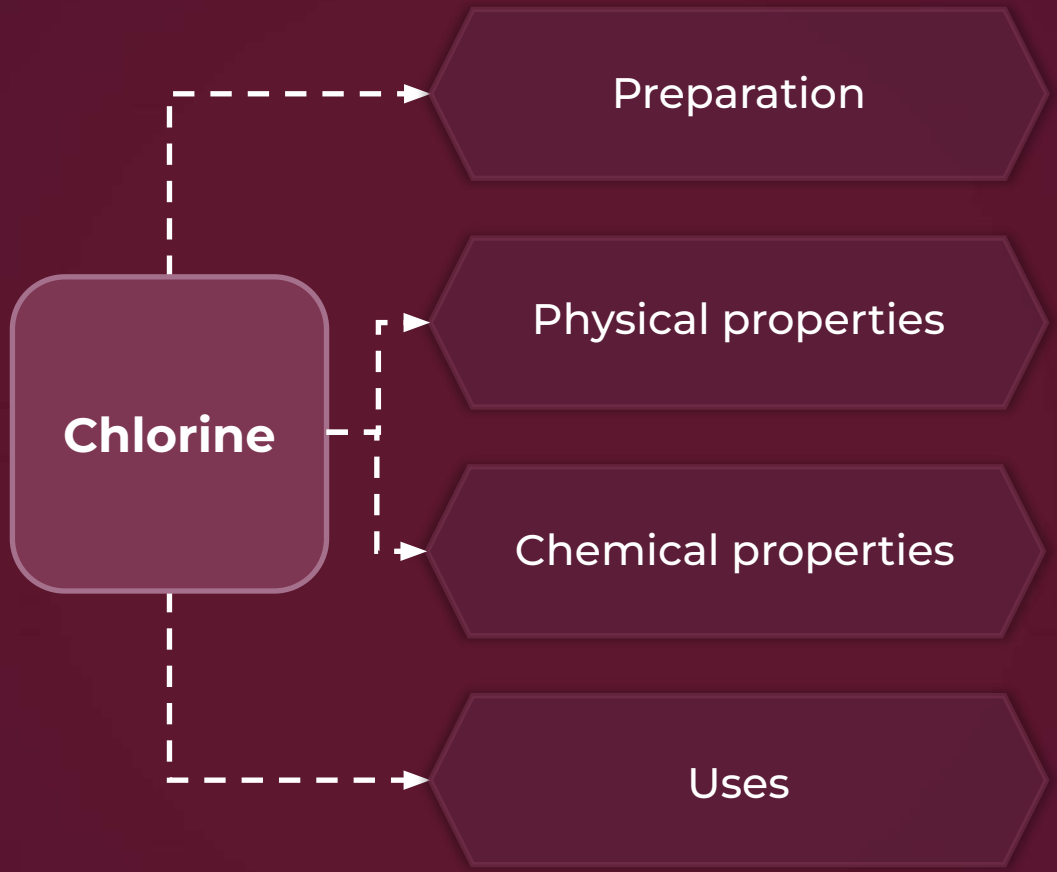
$$nX_2 + 2M \longrightarrow 2MX_n$$

Where M = Monovalent metal

Example

$$Br_2\ (\ell) + Mg\ (s) \longrightarrow MgBr_2\ (s)$$

If a metal exhibits **more than one oxidation state**, the halides in higher oxidation state will be **more covalent** than the one in lower oxidation state.


Chlorine
Preparation
Physical properties
Chemical properties
Uses

Preparation of Chlorine

1. By heating manganese dioxide with concentrated hydrochloric acid

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

2. Air is used to **oxidise HCl** in the presence of $CuCl_2$ (catalyst) at 713 K.

$$HCl + O_2 \xrightarrow[440\ ^oC]{CuCl_2} 2Cl_2 + 2H_2O + Heat$$

Reaction is **reversible**, and the conversion is **65%**

Physical Properties of Cl_2

01 Greenish yellow gas with **pungent** and **suffocating odour**

02 About **2–5 times** heavier than air

03 **Soluble** in water

Chemical Properties of Chlorine

Chlorine reacts with a number of **metals** and **non-metals.**

$$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$

Cold and dil.

$$6NaOH + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$

Hot and conc.

Chlorine water on standing loses its **yellow colour** due to the formation of **HCl** and **HOCl.**

HOCl gives **[O],** which is responsible for the **oxidising** and **bleaching** properties of chlorine.

Chemical Properties of Chlorine

Oxidising property

$$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$

$$I_2 + 6H_2O + 5Cl_2 \longrightarrow 2HIO_3 + 10HCl$$

Chlorine is a **powerful bleaching agent(due to nascent oxygen)** and the bleaching effect is **permanent**

$$Cl_2 + H_2O \longrightarrow 2HCl + [O]$$

Coloured Substance $\xrightarrow{[O]}$ Colourless substance

Phosgene

Preparation

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$

Properties

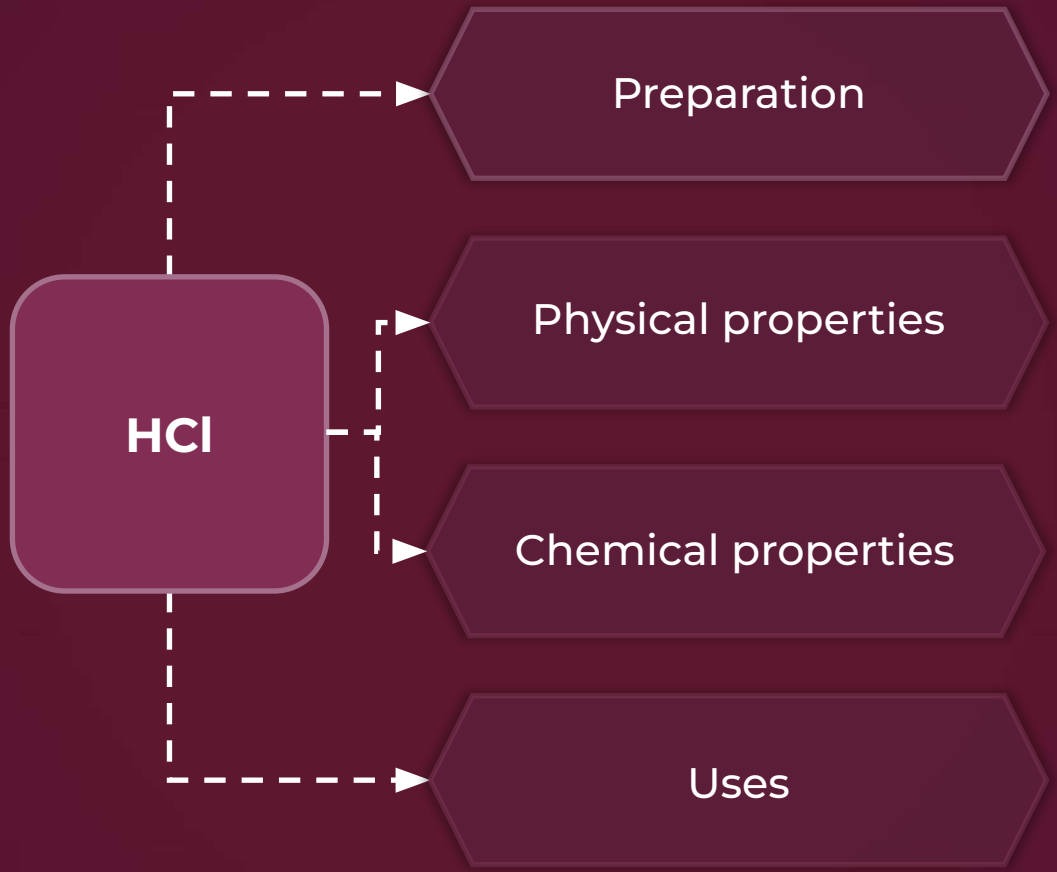
01 **Highly** toxic **colourless** gas.

02 **Planar** geometry

03 **Slightly soluble** in water

Uses of Chlorine

- Bleaching
- Preparation of poisonous gases such as phosgene ($COCl_2$), tear gas(CCl_3NO_2) and mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$)etc.


HCl
Preparation
Physical properties
Chemical properties
Uses

Preparation of HCl

Heating sodium chloride with concentrated sulphuric acid

$$NaCl + H_2SO_4 \xrightarrow{150^\circ C} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{550^\circ C} Na_2SO_4 + HCl$$

Physical Properties of HCl

Colourless, pungent smelling gas at room temperature.

Quiet **soluble** in water

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

Physical Properties of HCl

The aqueous solution is called **hydrochloric acid.**

High value of dissociation constant (K_a)

Strong acid in water

$K_a \approx 10^7$

Chemical Properties of HCl

- **Acidic character:**

  It reacts with NH_3 and gives off **white fumes** of NH_4Cl

$$NH_3 + HCl \longrightarrow NH_4Cl$$

- Hydrochloric acid decomposes the **salts** of **weak acids.**

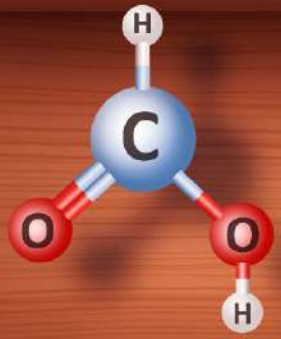
$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

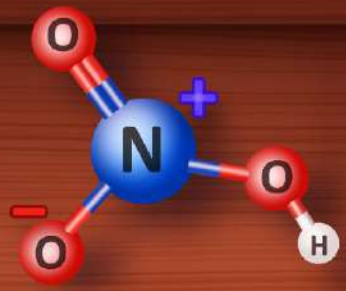
$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

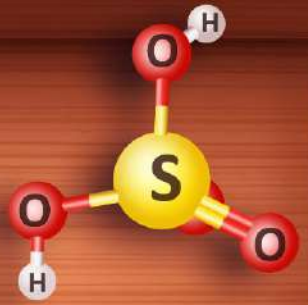
$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$$

Uses of SO_2

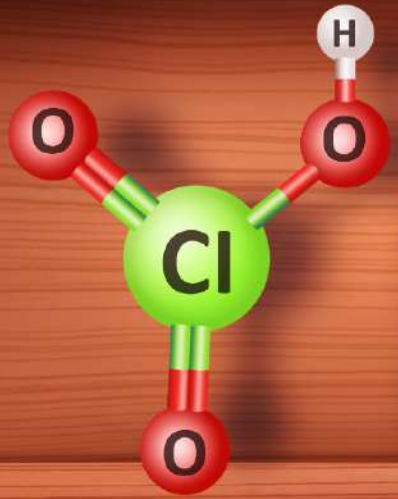
- In manufacturing chlorine, NH_4Cl, and glucose (from corn starch)
- In medicines
- As a laboratory reagent

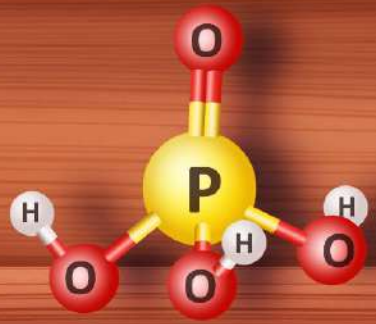






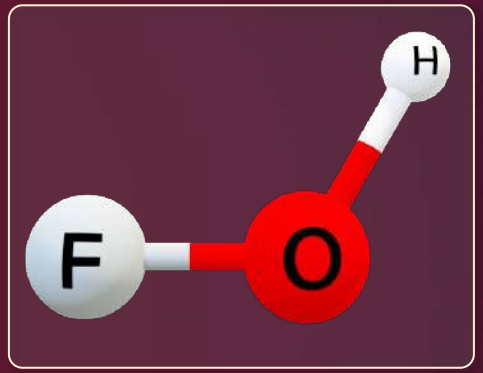
OXO-ACIDS





Oxoacid of Fluorine

Hypofluorous acid (HOF)

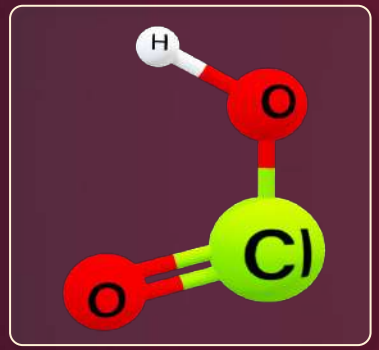


Fluorine is unique among the halogens in forming no species in which it has a formal oxidation state other than **-1.**

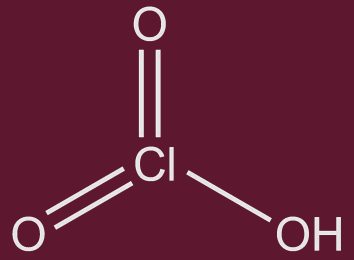
The only known oxoacid is **hypofluorous acid, HOF.**

Oxoacids of Chlorine

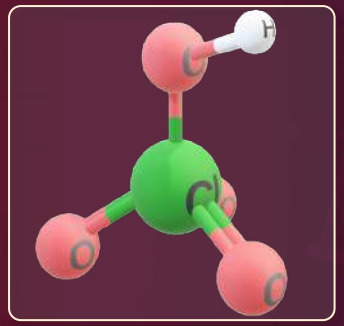
Chlorous acid

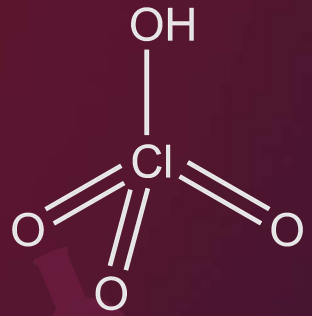


Chloric acid



Perchloric acid





Interhalogen Compounds

Halogen atoms have different electronegativity. Due to this **difference** in electronegativity, the halogen atoms combine with each other.

This gives rise to the formation of covalent compounds, which are called **interhalogen** compounds.

Types and Examples of Interhalogen Compounds

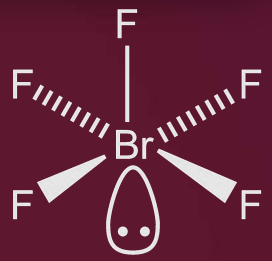
1. There are four types of interhalogen compounds: XX', XX'_3, XX'_5, and XX'_5. Where, X and X' are halogen of larger size and smaller size respectively.

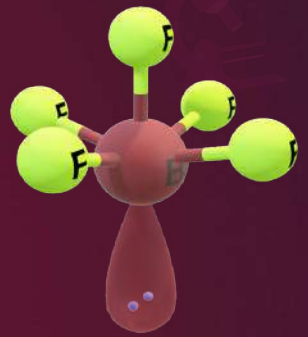
2. X is more electropositive than X'

3. Examples: Iodine monofluoride (IF), chlorine trifluoride (ClF_3), bromine pentafluoride (BrF_5).

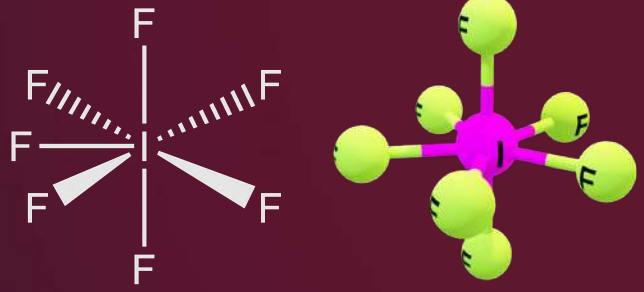
Types and Examples of Interhalogen Compounds

Iodine monofluoride

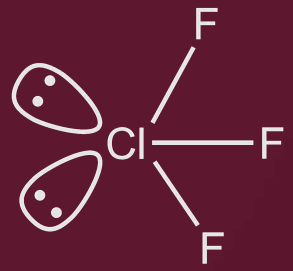


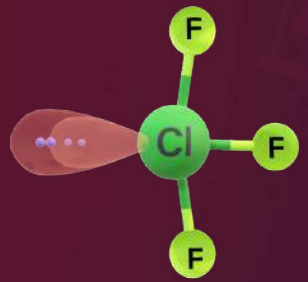


Bromine pentafluoride



Iodine heptafluoride





Chlorine trifluoride

Interhalogen Compounds

$$\frac{\text{Radii of X}}{\text{Radii of X'}} \uparrow$$

Number of atoms per molecule ↑

Thus, iodine (VII) fluoride should have the **maximum number of atoms** as the ratio of the radii between I and F should be the **maximum**.

That is why its formula is **IF_7** (having the maximum number of atoms).

Preparation

By the **direct combination** of halogens:

$Cl_2 + F_2$ (equal volumes) $\xrightarrow{473\ K}$ $2ClF$

$Cl_2 + 3F_2$ (excess) $\xrightarrow{573\ K}$ $2ClF_3$

$I_2 + Cl_2$ (equimolar) $\longrightarrow$ $2ICl$

$IF_5 + I_2 \xrightarrow{543\ K} IF_7$

$BrF_3 + F_2$ (excess) $\longrightarrow$ BrF_5

Physical Properties

1 These compounds may be **gases, liquids,** or **solids.**

Gases: ClF, BrF, ClF_3, IF_7

Liquids: BrF_3, BrF_5

Solids: ICl, IBr, IF_3, ICl_3

2 All interhalogens are **covalent molecules** and are **diamagnetic** in nature.

3 Electronegativity difference $\propto$ Boiling point

between
X and X' atoms

Physical Properties

4

Electronegativity difference $\propto$ Thermal stability

XX' type

between X and X' atoms

IF > ClF > ICl

More polar is the X–X' bond, more is the **stability of interhalogen**.

Chemical properties of interhalogen compounds

1. Interhalogen compounds are more reactive than the parent halogens but less reactive than F_2.
2. X–X' bond in interhalogens is weaker than the X–X bond in halogens, except for F-F bond.
3. Polarity of the bonds make it more susceptible for the other reactions.
4. All Interhalogen compounds undergoes hydrolysis.

$$AB + H_2O \longrightarrow HB + HOA$$

Chemical Properties

A halide ion from smaller halogen and a **hypohalite** (when **AB**) anion derived from larger halogen.

$AB + H_2O \longrightarrow HB + HOA$

$BrCl + H_2O \longrightarrow HCl + HOBr$

$ICl + H_2O \longrightarrow HCl + HIO$

A halide ion from smaller halogen and a **halite** (when AB_3), **halate** (when AB_5) anion derived from larger halogen.

$ICl_3 + 2H_2O \longrightarrow 3HCl + HIO_2$

$IF_5 + 3H_2O \longrightarrow 5HF + HIO_3$

$BrF_5 + 3H_2O \longrightarrow 5HF + HBrO_3$

Chemical Properties

A halide ion from smaller halogen and a **perhalate** (when AB_7) anion derived from larger halogen.

$$IF_7 + 6H_2O \longrightarrow 7HF + H_5IO_6$$

Uses of Interhalogen compounds

Interhalogen compounds are very useful **fluorinating agents.**

Enrichment of uranium ore

$$U\,(s) + 3ClF_3\,(\ell) \longrightarrow UF_6\,(g) + 3ClF\,(g)$$

Group 18 Elements

- Helium
- Neon
- Argon
- Krypton
- Xenon
- Radon

All these are gases and are chemically **unreactive.**

They **form very few compounds**, and hence they are termed as **noble gases.**

Occurrence and Isolation

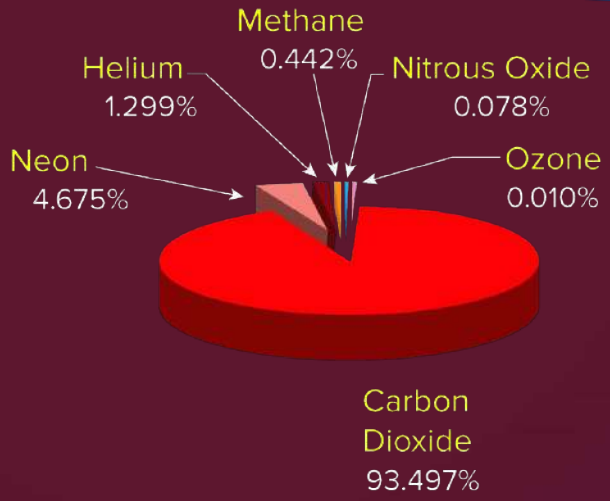
All noble gases present in the atmosphere

Except radon

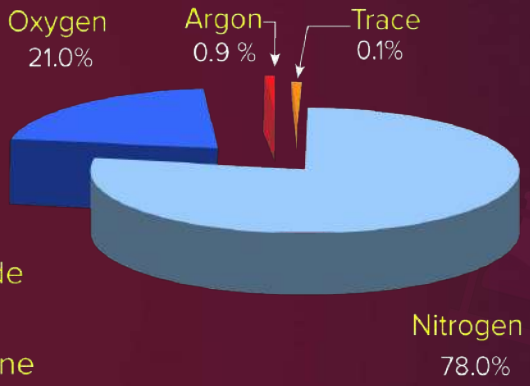
Order of abundance in air

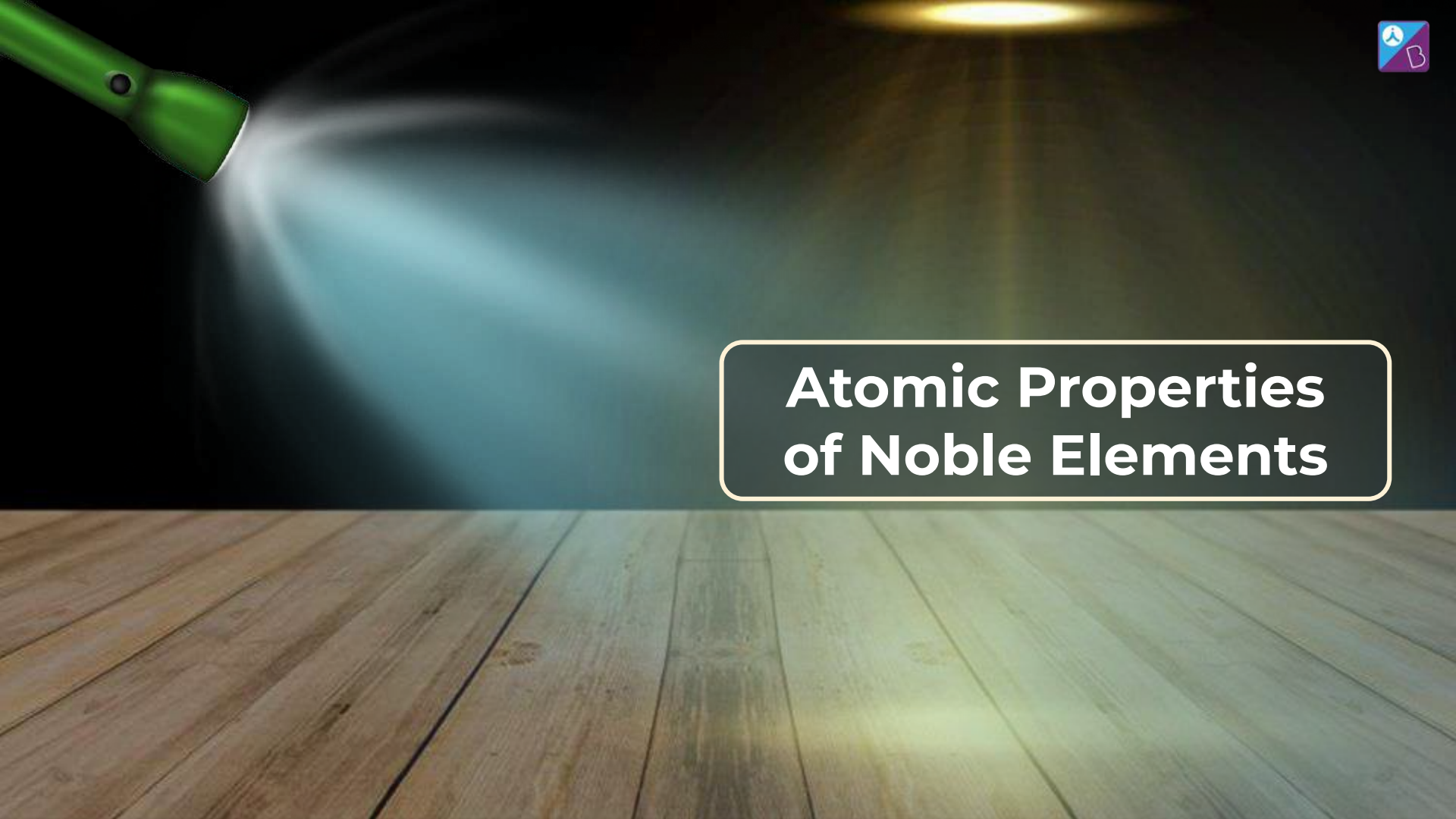
Ar > Ne > Kr > He > Xe

Trace Gases



Atmospheric Composition




Atomic Properties
of Noble Elements

Atomic Properties

Electronic configuration

All noble gases have the general electronic configuration ns^2np^6.

Except **Helium ($1s^2$)**

Their inactive nature are ascribed to their **completely filled electronic configuration**.

Atomic radii

Down the group

Increases

Reason Number of shells increases

He < Ne < Ar < Kr < Xe

Atomic Properties

Ionisation enthalpy

Due to the stable electronic configuration, they exhibit **very high ionisation enthalpy.**

Down the group — Decreases

He > Ne > Ar > Kr > Xe

Physical Properties

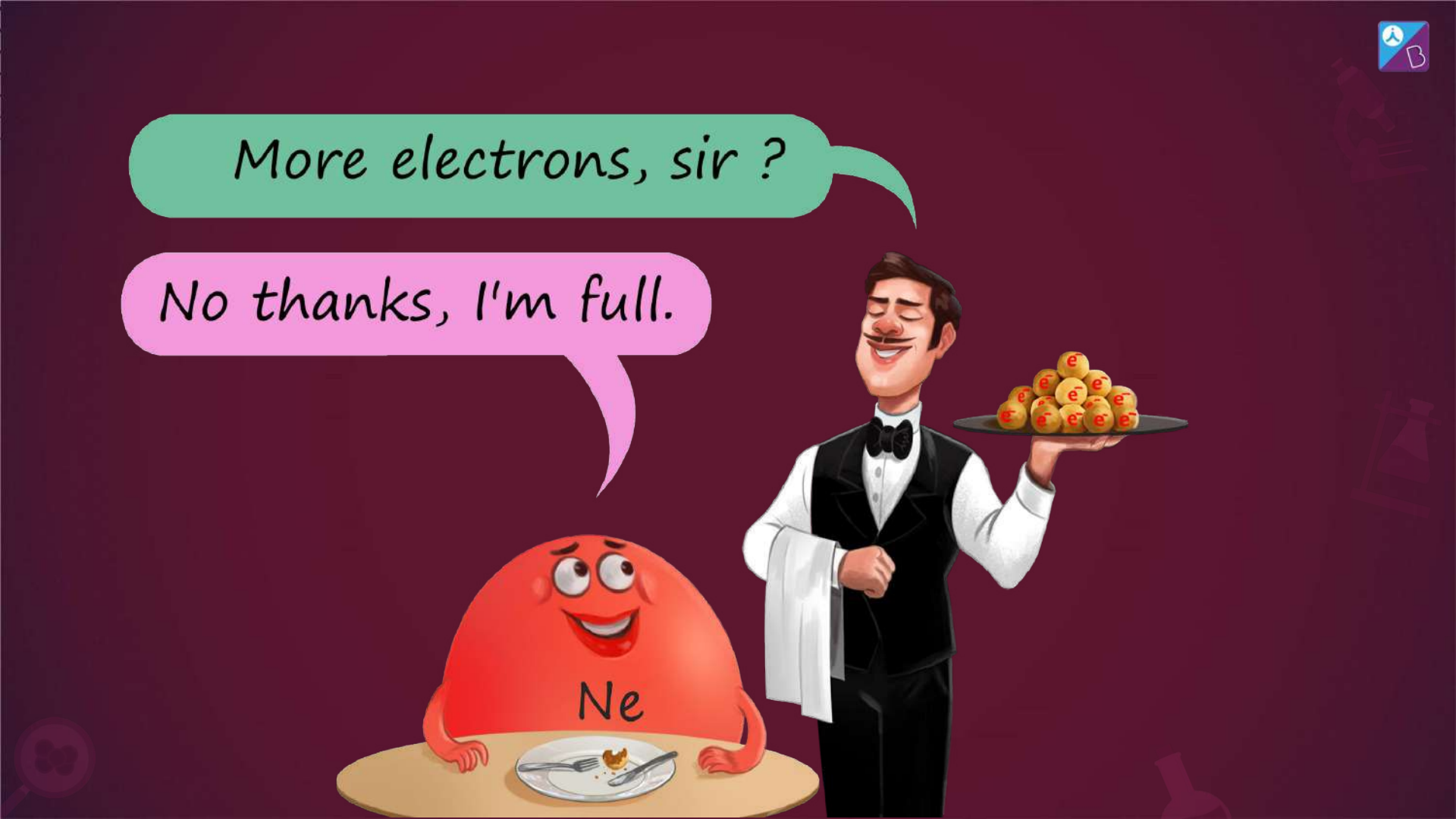
1. All the noble gases are **mono-atomic**.
2. **Colourless**, **odourless**, and **tasteless**.
3. **Sparingly** soluble in water.
4. **Very low** melting and boiling points

This is because the only type of **interatomic interaction** in these elements is **weak dispersion forces.**

Chemical Properties

Noble gases are **least reactive due to**

- Completely **filled ns^2 np^6** electronic configuration in their valence shell
- **High ionisation enthalpy** and more **positive electron gain enthalpy**


More electrons, sir ?
No thanks, I'm full.
Ne

Reactivity of Noble Gas

The compounds of krypton are fewer. Only the **difluoride (KrF_2)** has been studied in detail.

No true compounds of Ar, Ne or He are yet known.

Neil Bartlett

UBC 1962

Reactivity of Noble Gas

Neil Bartlett prepared a red compound which is formulated as $O_2^+PtF_6^-$

He observed that,

$(I.E._1)_{O_2}$ ≈ $(I.E._1)_{Xe}$

1175 kJ/mol

1170 kJ/mol

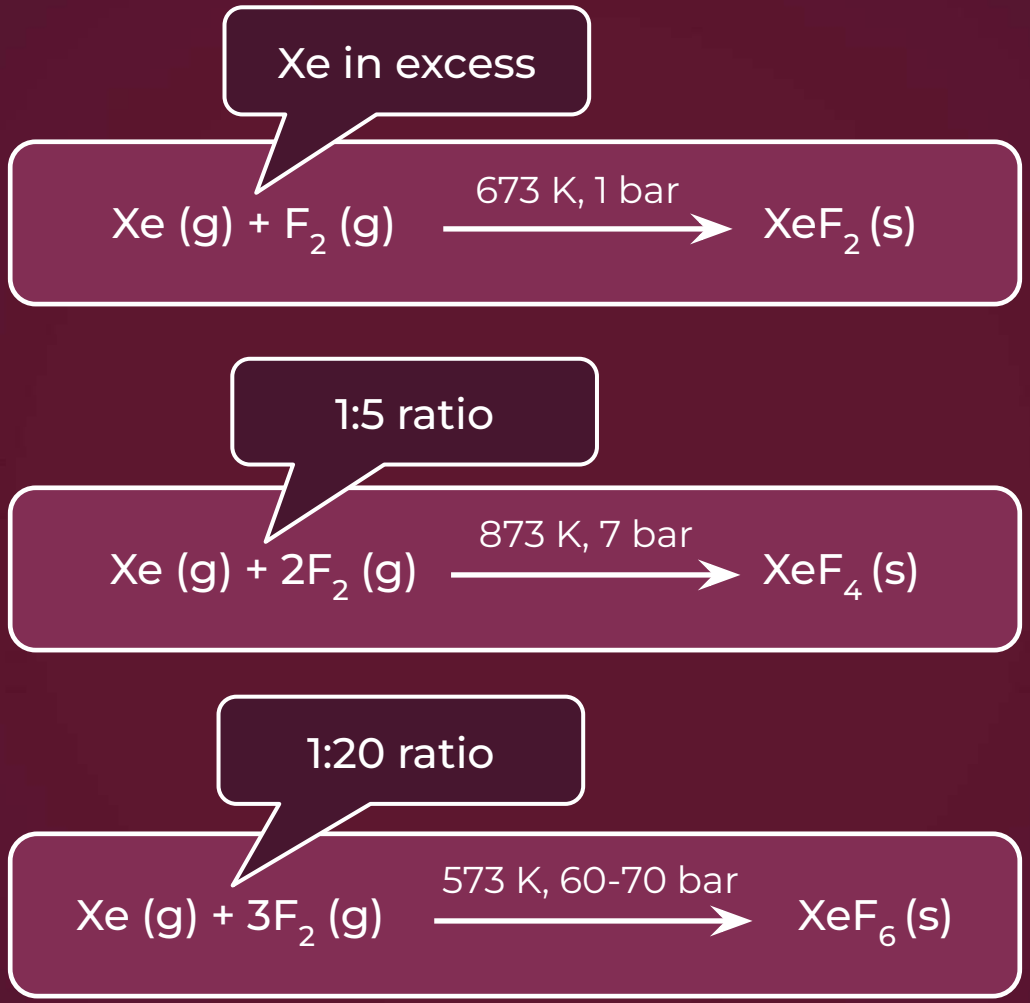
He also prepared another red coloured compound with $Xe^+PtF_6^-$ by mixing PtF_6 and xenon.

A number of xenon compounds, mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

Preparation of Xenon Fluoride Compound

Xenon forms three binary fluorides, namely **XeF_2, XeF_4, and XeF_6,** by the direct reaction of elements under appropriate experimental conditions.

The products formed depend on the **Xe/F_2 ratio.**


Xe in excess
Xe (g) + F2 (g)
673 K, 1 bar
XeF2 (s)
1:5 ratio
Xe (g) + 2F2 (g)
873 K, 7 bar
XeF4 (s)
1:20 ratio
Xe (g) + 3F2 (g)
573 K, 60-70 bar
XeF6 (s)

Properties of Xenon Fluoride Compound

- XeF_2, XeF_4, and XeF_6
- **Colourless** crystalline solids
- They are **readily hydrolysed** even by traces of water
- Powerful **fluorinating agents**

Properties

Xenon fluorides react with

- Fluoride ion **acceptors** to form **cationic species**
  - $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$
- Fluoride ion **donors** to form **fluoroanions**
  - $XeF_6 + MF \longrightarrow M^+[XeF_7]^-$

(M = Na, K, Rb or Cs)

Structure of Xenon-Fluoride Compounds

Compound	Hybridisation	Geometry	Shape
XeF_2	sp^3d	Trigonal bipyramidal	Linear
XeF_4	sp^3d^2	Octahedral	Square planar
XeF_6	sp^3d^3	Pentagonal bipyramidal	Distorted octahedron

Preparation of Xenon Oxygen Compound

1. Hydrolysis of XeF_4 and XeF_6 gives **XeO_3**.

$$4XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

2. Partial hydrolysis of XeF_6 gives oxyfluorides, **$XeOF_4$, and XeO_2F_2**.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

Properties of Xenon Oxygen Compound

Compound	Physical properties	Molecular structure
XeO_3	Colourless, explosive solid	Pyramidal
$XeOF_4$	Colourless, volatile liquid	Square pyramidal

Uses of Noble gases

Helium is used in filling balloons and in gas -cooled nuclear reactors.

Neon is used in fluorescent bulbs and discharge tubes.

Argon is used in filling electric bulb and in arc welding.